THE SECOND LAW

P. W. Atkins

Scientific American Books
An imprint of W. H. Freeman and Company
COLLAPSE INTO CHAOS

Matter consists of atoms. That is the first step away from the superficialities of experience. Of course, we could burrow even further beneath superficiality, and regard matter as consisting of more (but perhaps not limitless more) fundamental entities. Perhaps Kelvin was right in his suspicion that the most fundamental aspect of the world is its eternal, elusive, and perhaps zero energy. But although the onion of matter can be peeled beyond the atom, that is where we stop for in thermodynamics we are concerned with the changes that occur under the gentle persuasion of heat, and under most of the conditions we encounter, the energy supplied as we heat a system is not great enough to break open its atoms. The gentleness of the domain of thermodynamics is why it was among the first of scientists’ targets: only as increasingly energetic methods of exploration and destruction became available were other targets opened to inspection, and in turn, as the vigor of wars increased, so the internal structure of the atom, the nucleus, and the nucleons became a part of science. Heat, although it may burn and sear, is largely gentle to atoms.

The concept of the atom, although it originated with the Greeks, began to be convincing during the early nineteenth century, and came to full fruition in the early twentieth. As it grew, there developed the realization that although thermodynamics was an increasingly elegant, logical, and self-sufficient subject, it would remain incomplete until its relation to the atomic model of matter had been established. There was some opposition to this view; but support for it came from (among others) Clausius, who identified the nature of heat and work in atomic terms, and set alight the flame that Boltzmann soon was to shine on the world.

Although we have been speaking of atoms, in many of the applications of thermodynamics molecules also play an important role, as do ions, which are atoms or molecules that carry an electric charge. In order to cover all these species, we shall in general speak of particles.
Inside Energy

As a first step into matter we must refine our understanding of energy by recalling some elementary physics. In particular, we should recall that a particle may possess energy by virtue of its location and its motion. The former is called its potential energy, the latter is its kinetic energy.

A particle in the Earth's gravitational field has a potential energy that depends on its height: the higher it is, the greater its potential energy. Likewise, a spring has a potential energy that depends on its degree of extension or compression. Charged particles near each other have a potential energy by virtue of their electrostatic interaction. Atoms near each other have a potential energy by virtue of their interaction (largely the electrostatic interactions between their nuclei and their electrons).

A moving particle possesses kinetic energy: the faster it goes, the greater its kinetic energy. A stationary particle possesses no kinetic energy. A heavy particle moving quickly, like a cannonball (or, in more modern terms, a proton in an accelerator), possesses a great store of energy in its motion.

The most important property of the total energy of a particle (the sum of its potential and kinetic energies) is that it is constant in the absence of externally applied forces. This is the law of the conservation of energy, which moved to the center of the stage as the importance of energy as a unifying concept was recognized during the nineteenth century. It accounts for the motion of everyday particles like baseballs and boulders, and applies to particles the size of atoms (subject to some subtle restrictions of that great clarifier, the quantum theory). For instance, the law readily accounts for the motion of a pendulum: there is a periodic conversion from potential to kinetic energy as the bob swings from its high, stationary turning point, moves quickly (with high kinetic energy) through the region of lowest potential energy (at the lowest point of its swing), and then climbs more and more slowly to its next turning point. Potential and kinetic energy are equivalent, in the sense that one may readily be changed into the other; their sum, in an isolated object, remains the same.

Intrinsic to the soul of thermodynamics is the fact that it deals with vast numbers of particles. A typical yardstick to keep in mind is Avogadro's number. Its value is about $6 \times 10^{23}$, and it represents the number of atoms in 12 grams of carbon. (By coincidence, it is not far off the number of stars in all the galaxies in the visible Universe.) The idea to appreciate here is not the precise value of Avogadro's number, or the precise number of atoms in any given system, but the fact that the numbers of atoms involved in everyday samples of matter are truly enormous. It may seem surprising at first sight that science learned to deal with the properties of such enormous crowds of particles before it discovered how to deal with individual atoms. The reason lies at the core of thermodynamics: the thermodynamic properties of a system are energy values over statistically large assemblies of particles. Just as it is easier to deal with average properties of human populations than with individuals, so it is easier to deal with the average properties of assemblies of particles than with the individuals. Idiosyncrasies (which the atomically aware thermodynamicist terms fluctuations) are ironed out and become relatively insignificant when the populations are large, and the population of particles in a typical sample is vastly greater than the population of people of any nation.

The energy of a thermodynamic system, such as the several Avogadro's numbers of water molecules in a glass of water, is the sum of the kinetic energies of all the particles and of their potential energies too. Hence, it should be plain that this total energy is constant (the essential content of simple versions of the First Law). However, in a many-particle thermodynamic system, a new aspect of the motion, one not open to a single particle on its own becomes available.

Consider the kinetic energy of the collection. If all the particles happen to be traveling in the same direction with the same speed, then the entire system is in flight, like a baseball (see below). The entire system behaves like a single, massive particle, and the ordinary laws of dynamics apply.

However, there is another sort of motion. Instead of all the particles moving uniformly, we can think of them as being chaotic: the total energy of the system may be the same as that of the ball in flight, but now there is no net motion, because all the directions and speeds of the atoms are jumbled up in chaos (see the figure on the next page). If we could follow any
The same quantity of energy may be stored by a stationary but warm ball. Now the particles are moving incoherently; they are turned ON. The random, incoherent motion is called thermal motion.

A couple of examples should make this clear. Suppose we want to change the energy of a 1-kilogram block of iron (a cube about 5 cm on each side). One way would be to lift it; lifting it through 1 meter increases its potential energy by about 10 joules (Appendix I). What have we done is move all its atoms coherently through a displacement of 1 meter. Energy has been transferred to the block, and is now stored in the gravitational potential energy of all its atoms. Energy has been transferred by doing work.

Suppose instead that the block is hurled off in some horizontal direction. Now the kinetic energy of all its atoms has been increased and their motion is coherent. If they all move at 4.5 meters per second (about 10 m per h), the block acquires 10 joules of energy. Energy has been transferred to the block, and is now stored in the kinetic energy of all its atoms. Once again, energy has been transferred by doing work.

Now suppose we expose the block to a flame, and raise its temperature. This increases its energy, but the block remains in its initial position and seems not to be moving. However, if the temperature is raised by only 0.03 °C, the transfer will correspond to 10 joules of energy, exactly as before. Now the energy is stored in the thermal motion of the atoms. It is still stored as their kinetic and potential energies (the only form of energy storage we ever need consider), but now the locations and motions of the atoms are incoherent, and there is no net displacement or motion of the block as a whole. Energy has been transferred to the block by stimulating the incoherent motion of its atoms. Energy has been transferred by heating the block.

This distinction is illustrated above.

individual particle, we would see it moving a tiny amount to the right, bouncing off its neighbor, moving to the left, bouncing again, and so on. The central feature is the lack of correlation between the motions of different particles: their motion is incoherent.

This random, chaotic, uncorrelated, incoherent motion is called thermal motion. Obviously, since it is meaningless to speak of the uncorrelated motion of a single particle, the concept of thermal motion cannot be applied to single particles. In other words, when we step from considering a single particle to considering systems of many particles, when the question of coherence becomes relevant, we are stepping out of simple dynamics into a new world of physics. This world is thermodynamics. All the richness of the subject, the way that the steam engine can make the journey into life and account for the unfolding of a leaf, results from this enlargement of domain.

We have established that there are two modes of motion for the particles of a composite system: the motion may be coherent, when all the particles are in step, or the motion may be incoherent, when the particles are moving chaotically. We have also seen in our encounter with the First Law that there are two modes of transferring energy to a system, by doing work on it or by heating it. Now we can put the remarks together:

When we do work on a system, we are stimulating its particles with coherent motion; when the system is doing work on the surroundings, it is stimulating coherent motion.

When we heat a system, we are stimulating its particles with incoherent motion; when a system is heating its surroundings, it is stimulating incoherent motion.
The Mark I universe. Each rectangle represents an atom; there are 1,600 in all.

Modeling the Universe

The Universe is quite a complicated place, but there are a lot of simple things going on inside it. In much of the following discussion, it will prove useful to focus on the essential features of the processes without getting distracted by complications like dogs, opinions, and other trappings of reality. Of course, we must always ensure that the simplification doesn’t destroy important details; so we shall swing frequently between the very simple models of the Universe and the actual Universe, in which simplicities are sometimes so cloaked in consequences that their true natures are obscured. When we refer to a model of the Universe, we shall call it a “universe.”

We shall use two simple models of the Universe. The Mark I universe consists of up to 1,600 atoms (see above).* Each atom may be energetically unexcited, which we shall call OFF, or energetically excited, which we shall call ON. In the illustrations we shall denote ON-ness by a red blob (see figure on left). When several atoms are ON, we shall take their motions to be uncorrelated unless specified. That is, several red blobs in the region of the universe that represents some system means that the atoms are storing their energy as thermal motion. When we want to indicate that the motion of a group of atoms is coherent, we shall say that the atoms are ON* and denote them by red arrows in the direction of their motion (see figure on left). Another simplifying feature of the Mark I universe is that each atom can possess only a single characteristic energy when it is ON, and this quantity is the same for each atom. (We could think of the energy required to turn an atom ON as being 1 joule, although that would correspond to a cannonball of an atom. If a hydrogen atom is supplied with only $10^{-18}$ joules, it falls apart. The actual value will not be important for most of what follows; so we can adopt the simplest value in order to have something concrete, or just leave it unspecified if something more concrete is not needed.)

The Mark II universe is the same as the Mark I version, except that the number of atoms in it is infinite: we can still use the 1,600 blobs to show atoms, but now this represents only a minute fraction of the total universe (see below). This is the universe we use when we want to model the reservoirs we mentioned in Chapter 2: they are inextinguishable inexhaustible sources.

The Mark III universe (see figure on next page) we shall hold in reserve for now: it has more complicated entities, such as atoms that can possess various quantities of energy, atoms of different kinds, concatenations of atoms, and even people.

* The universe has been given this number of atoms for a special reason: 1,600 is the number of pixels on a low-resolution graphics screen of an Apple computer. The illustrations that follow, and the calculations behind some of the numbers, have been prepared on an Apple IIe. Some of the positive programs used are listed in Appendix 1. By using them, you will be able to explore the properties of the universe in the manner we shall gradually unfold.
The Mark III universe is much more complicated; it has all sorts of atoms strong together in complex patterns. Nevertheless, the underlying process is no more complex than the ones possessed by the earlier Marks.

Now we put the Mark I universe into operation and see what it reveals about the process of change. The only rule we shall impose is the conservation of energy in the universe as a whole (so that the number of atoms ON remains constant). We shall allow any atom to hand on its ON-ness to a neighbor, or pick up energy, and so turn ON, from a neighbor that happens to be ON already. (An atom cannot be more than ON or partially ON: one ON per atom at most, and either ON or OFF.)

In terms of an actual process in the Universe, we can think of the gray area in the figure on the facing page as representing one block of iron, and the unshaded area as representing another. Then the state of being ON represents an atom that is vibrating vigorously around its average location, and an atom that is OFF represents an atom that is motionless. The handing on of ON-ness then corresponds to an ON atom jostling a previously motionless neighbor, which breaks into vibration at the expense of the energy of the previously vibrating atom. This handing on of vibrational motion is a random process, and so ON-ness just wanders at random from atom to atom.

The central point about the behavior of the universe, and by extension of the Universe too, is that properties arise from the minimum of rules. The only rule we are adopting is the conservation of ON-ness. We are allowing undirected and unconstrained mobility. Even with this light touch, the universe possesses properties. The same properties could be obtained by imposing rules, such as the rule that energy shall migrate from atom to atom in a specified manner. But such rules are plainly unnecessary, and the scientific razor cuts them out.

Suppose we have the arrangement of ON-ness in the universe as depicted above. This corresponds to a lot of energy stored in the thermal motion of System 1 (one block of iron), and none at all in System 2 (the other block). What will happen?

As the excited atoms of System 1 wobble, they bump into each other, and any one can pass its energy on to any of its neighbors. If this happens, then the first atom turns OFF, and the second turns ON. The newly ON atom is itself now wobbling and jostling its neighbors, and so it may exchange energy with them. The energy, the ON-ness, therefore wanders aimlessly through the system and may arrive at its edge.

At the edge where System 1 touches System 2, the jostling takes place just as it does inside the system itself. An excited atom on the face of System 1 can jostle an atom on the face of System 2, and turn the latter ON. This ON atom jostles its neighbors, and so the energy migrates at random into and through System 2. In this way the thermal motion of the atoms in System 2 is stimulated, but at the expense of System 1. That is, System 2 is heated by System 1, and the latter cools (see top figure on next page).
Some time after the initial stage, the energy is spread more uniformly over all the atoms as a result of their jostling each other. The small block still has a higher proportion of its atoms ON than the bigger block, and so it is still hotter. The temperature of System 1 is now 0.72 and that of System 2 is 0.23.

What is the final state of the universe? There is no final state for the careful observer, for the ON-ness jostles and migrates forever (there is no rule that brings it to an end). But there is an apparent final state for an observer who stands so far back that the behavior of the individual atoms cannot be discerned. There is a final state for the thermodynamic observer, not for the atomic individualist. This apparent end of change occurs when there is a uniform distribution of ON-ness, as in the figure below.

Later, the jostling of the atoms results in a uniform distribution of the energy. There will be small areas wherein there are ON and off areas (there are fluctuations), but on average the proportion of atoms ON in the smaller block is equal to the proportion ON in the larger. The temperatures of the blocks are now the same, at 0.27, and they are at thermal equilibrium.

The sequence of illustrations on the two preceding pages shows how the universe attains not so much a final state as a steady state. In this state the individual atoms turn ON and OFF as they have always done, but, to the casual observer of averages, the redistribution of energy leaves the universe apparently unchanged. We see that the jostling, random migration of energy disperses it. When it is uniformly dispersed over the available universe, it remains dispersed.

That last remark is not quite true, because the random wandering of ON-ness may lead it to accumulate, by chance, in System 1 and leave System 2 completely OFF. However, even with a universe of 1,600 atoms this chance is slight (as may be tested by using one of the programs), and in a real Universe, where each system is a block of Avogadro's numbers of atoms, the chance is so remote that it is negligible. Lack of rules allied with vastness of domain accounts for the virtual irreversibility of the process of dispersal.

**Temperature**

Before we wrap this observation into a neat package, let us notice that we are also closing in on the significance of temperature. We have just seen that System 1 heats System 2 as a natural consequence of the dispersal of energy, and that the net transfer of energy continues until, on average, the energy is evenly dispersed over all the available atoms. Now note the following important distinction. When the ON-ness is evenly distributed, there is more energy in System 2 than in System 1 (because the former contains more atoms, and therefore more are ON when the ON-ness is uniformly distributed), but the ratio of the numbers ON and OFF is the same in both.

All this conforms with common sense about hot and cold so long as we interpret the ratio of the numbers of atoms ON and OFF as indicating temperature. First, we know that energy flows as heat from high temperatures to low, and we have seen that System 1 (which initially has a higher "temperature" than System 2) heats System 2. Second, the steady state, when there is no net flow of energy between the two systems, corresponds to their having equal "temperatures," not equal total energies. Finally, "temperature" measures the incoherent motion, not the coherent motion, of particles; it is intrinsically a thermodynamic (as distinct from a dynamic) property of systems of many particles. It would be absurd to refer to the temperature of a single particle. When we say that a baseball is warm, we are referring to the excitation of its component particles, not to the whole baseball regarded as a single particle.
Temperature reflects the ratio of the numbers of atoms ON and OFF; the higher the ratio, the higher the temperature. This interpretation carries over into the actual Universe, where high temperatures correspond to systems in which a high proportion of particles are in excited states. Notice once again the sharp distinction between the temperature of a system and the energy it may possess: a system may possess a large quantity of energy, yet still have a low temperature. For instance, a very large system may have a low proportion of its atoms ON, and therefore be cool, but there are still so many atoms that the sum of their energies is large, and so overall the system possesses a lot of energy. The oceans of the Earth, although they are cool, are immense storerooms of energy. The energy of a system depends on its size; the temperature does not.

A further point is more in the nature of housekeeping. The concept of temperature entered thermodynamics along a classical route; it would be a remarkable piece of luck if the classical definition had turned out to be numerically the same as the ratio of numbers of ON to OFF. The best we can reasonably expect is that increasing temperature in the classical sense corresponds to increasing ratio of ON to OFF in the atomic sense. We cannot assume they will increase in precisely the same way; temperature might increase as the square (or some other increasing function) of the ratio, and not directly as ON/Number_OFF itself.

We have seen that classical thermodynamics, speaking about the efficiencies of engines, imposes a lower bound to temperature: there is an absolute zero of temperature. In the atomic interpretation, we would expect this to correspond to a system in which no atoms at all are ON (as in the initial state of System 2, depicted in the figure on page 53). Since there cannot be fewer than no atoms ON, the atomic approach to temperature neatly corroborates the classical expectation of a lower bound to temperature. This is just one example of how the atomic interpretation leads to straightforward explanations of classical conclusions.

It turns out that the thermodynamic and atomic versions of temperature coincide in all respects—the temperature goes up if the ratio goes up; the temperature is zero if no atoms are ON; the thermodynamic expressions relating temperature, energy, and entropy all work—if temperature is related to the ratio by

\[ T = \frac{A}{\ln(Number_{ON})/Number_{OFF}} \]

where \( A \) is a constant that depends on how much energy is needed to turn an atom ON. If for convenience we arbitrarily set \( A \) equal to unity, then the temperatures given by this expression are pure numbers (we could choose \( A \) to have the units of kelvins, as described in Appendix 2, but that is an unnecessary complication here).

By evaluating the preceding formula for appropriate values of numbers ON and OFF, we can acquire temperatures to the states of the universe illustrated in the figures on pages 53 and 54. The important point to notice is that the temperatures of the two systems converge to a value intermediate between their two initial values. Then, once they have reached equality of temperature, there they remain, except for chance fluctuations, forever. Using the computer programs, we can in fact map the fluctuations: they are shown in the figure above. Sometimes they are quite large, especially for the smaller system (and so we would notice if jumping between hot and cold around some average temperature); but that is because the systems, and especially the fragment we are calling System 1, are so small. A much larger system would show far smaller fluctuations of temperature at equilibrium; an infinite system would show virtually none.

The Direction of Natural Change

In a very natural way, without imposing superfluous rules, and whitling regulations to the bone, we have arrived at an explanation of the direction of at least one natural change. We have stumbled across one wing of the Second Law. Simply by accepting that jostling atoms pass on their energy at random, we have accounted for one class of phenomena in the world. In fact, this identification of the chaotic dispersal of energy as the purposeless motivation of change is the pivot of the rest of the book. The Second Law is the recognition by external observers of the consequences of this purposeless tendency of energy.
A preliminary working statement of the Second Law in terms of the behavior of individual atoms is therefore that energy tends to disperse. (We shall refine the statement as we assemble more information.) This is not a purposeful tendency: it is simply a consequence of the way that particles happen to bump into each other and in the course of the collision happen to hand over their energy. It is a tendency reflecting uncontrolled freedom, not intention nor compulsion.

At this stage we have seen only the tip of the iceberg of the processes involved in natural change, but as we go on we shall increasingly come to recognize that the simple idea of energy dispersing accounts for all the change that characterizes this extraordinary world. When we grasp that energy disperses, we grasp the spring of Nature. It should also be more apparent now that the Second Law is a commentary about events that are intrinsically simpler than those treated by the First Law. The latter is concerned with establishing the concept of energy, something that (it seems to me) remains elusive even after we have analyzed it into its kinetic and potential contributions: after all, what are they? Perhaps that elusiveness is appropriate for a concept so close to the Universe's core. The Second Law, on the other hand, regards the energy as an established concept, and talks about its dispersal. Even though we might not comprehend the nature of energy, it is easy to comprehend what is meant by its dispersal.

The interpretation of the Second Law that we have now partially established relates to the Clausius statement, which denies the possibility that heat will travel spontaneously up a temperature gradient. The dispersal interpretation simply says that energy might by chance happen to travel in such a way that it ends up where there is already a higher proportion of atoms ON (see below), but the likelihood is so remote that we can dismiss it as impossible. But what of the Kelvin statement of the Second Law: how is dispersal related to the conversion of heat to work?

The steps involved in harnessing a bouncing ball for work. On the left, the ball and a weight rest on a warm table. The ball bounces up as the energy stored in the thermal motion of the particles of the table is converted to the energy of the ball. The weight raises the ball. When the ball falls, it raises the weight. The overall process is the raising of a weight (that is, work has been done) at the expense of some heat, which contradicts the Kelvin statement.

In order to capture the interconversion of heat and work, we have to remember their distinction: work involves coherent motion, heat involves incoherent motion. The atomic basis of the dissymmetry in their freedom to interconvert can be identified by thinking about a familiar example.

Think of a bouncing ball. Everyone knows that a bouncing ball eventually comes to rest. No reliable witness has ever reported, and almost certainly no one has ever observed, the opposite change, in which a resting ball spontaneously starts to bounce, and then bounces higher and higher. This would be contrary to the Kelvin statement, because if we caught the ball at the top of one of its bounces, we could attach it to some pulleys, and lower it to the ground (see below). In doing so we could extract its energy as work. Since that energy came from the warmth of the surface on which it was initially resting (because we are not questioning the validity of the First Law: this is Jack's game again), we would have succeeded in converting heat into work, and the ball is back where it began. That possibility is denied by the Kelvin statement. Therefore, if we can use the idea of the dispersal of energy to account for the absence of reliable reports of balls that spontaneously bounce more vigorously, we shall capture Kelvin as well as Clausius in our net.
A bouncing ball consists of a collection of coherently moving atoms. The bundle of atoms moves coherently upward, slows down, changes direction, and moves coherently downward. If the ball is warm, the atoms also possess energy by virtue of their thermal motion, but we need not trouble about that initially. The motion of the ball can be modeled in the universe as shown above.

In the collision when the ball strikes the table, energy is transferred between the two sets of atoms (and among the atoms of each set). As a result, the atoms of the ball reverse their direction, rise off the table, and climb away. As they do so, their kinetic energy converts to potential; the ball gradually slows, then turns, and drops again.

However, not all the kinetic energy that the ball possessed immediately before the collision remains in it in the form of coherent motion. Some of this energy jostles out while its atoms are in contact with those of the table, and even some that remains becomes randomized in direction. How this happens even in a head-on collision is illustrated in the figure on the left, which shows what to the ordinary observer seems to be head-on, in fact, on an atomic scale, involves various particles approaching each other over a wide range of angles, and so the motion is transferred in random directions. (A coherent motion as well as a chaotic motion, of the atoms of the table will also be stimulated, because at the point of contact of the ball the atoms are pushed together, and a band of compression travels through the solid. Nevertheless, this band of squashed atoms gets randomized as it moves, and in due course decays into thermal motion. A similar fate awaits the compression wave through the surrounding air, the wave that gives rise to the sound of the ball hitting the table.)

The upshot of this discussion is that each time the ball hits the table, the coherent motion of its atoms is slightly degraded into the thermal motion of its atoms and the atoms of the rest of the universe. This is shown by the atoms turning ON in the ball and the surface (denoted by the yellow blobs above). As they turn ON the coherent motion gradually turns OFF. Therefore, after each bounce the surface and the ball are a little warmer because the impacts have stimulated the thermal motion at the expense of the coherent. The coherent motion of the atoms of the ball gradually degrades into the incoherent motion of the atoms of the universe. If we wait long enough, all the original coherent motion will have degraded into incoherent motion, and that incoherent motion will be uniformly distributed throughout the universe. The slightly warmer ball will be at rest on the slightly warmer table; moreover, the ball and table will be at the same temperature, for the ON-ness will have dispersed uniformly. The kinetic energy of the ball has been dissipated in the thermal motion. Coherence has collapsed into incoherence.

The reverse of this sequence is exceedingly unlikely to occur naturally. We can think of the ball sitting on the warm table. Its atoms and those of the table are wobbling around their mean positions, and there is plenty of energy to send it flying up into the air. However, there are two reasons why the energy is not available.

One problem is that the energy is distributed over all the atoms of the universe. Therefore, in order for the ball to go flying off upward, a good proportion of the dispersed energy must accumulate in the ball. This is not particularly likely to occur, because the ON-ness of the atoms is wandering around at random, and the chance of enough of it being in the ball simultaneously is very slight. The length of time we would have to wait can be explored by using the Fluctuations program in Appendix 3, which runs through the random jostling of a universe like that shown above. In a real Universe, with so many atoms, we would probably need to wait a good
fraction of eternity before seeing even such an insignificant miracle as a spontaneously bouncing ball, and matter would almost certainly decay first.

But in fact the reasons go deeper, for the ball could be put on a hot surface. We have already seen that a 1-kilogram block of iron can rise 1 meter above the surface of the Earth if we transfer 10 joules of energy to it, and such a quantity of energy can readily wander in if the block stands on a slightly hotter surface. But even cool balls placed on hot surfaces do not rise spontaneously into the air. Why? Because the accumulation of energy in the ball, the ON-ness of its atoms, is only a necessary condition for it to be able to rise into the air: it is not a sufficient condition. In order for the ball to rise, the atoms must be not merely ON, but ON*; that is, the energy must be present as coherent motion of the atoms, not merely as incoherent thermal motion. Even if sufficient energy were to wander into the ball from the surroundings, it would be exceedingly unlikely to switch all the atoms ON* and induce coherent motion.

Now we are at the nub of the interpretation of the Kelvin statement of the Second Law. The concept of dispersal must take into account the fact that in thermodynamic systems the coherence of the motion and the location of the particles is an essential and distinctive feature. We have to interpret the dispersal of energy to include not only its spatial dispersal over the atoms of the universe, but the destruction of coherence too. Then energy tends to disperse captures the foundations of the Second Law.

Natural Processes

The natural tendency of energy to disperse—that is, to spread through space, to spread the particles that are storing it, and to lose the coherence with which the particles are storing it—establishes the direction of natural events. The First Law allows events to run contrary to common experience: under its rule alone, a ball could start bouncing at the expense of cooling, a spring could spontaneously become compressed, and a block of iron could spontaneously become hotter than its surroundings. All these events could occur without contravening the conservation of energy. However, none of them occurs in practice, because although the energy is present it is unavailable. Energy does not, except by the most extreme chance, spontaneously localize and accumulate in a large excess in a tiny part of the Universe. And even if energy were to accumulate, there is little likelihood that is would do so coherently.

Natural processes are those that accompany the dispersal of energy. In these terms it is easy to understand why a hot object cools to the temperature of its surroundings, why coherent motion gives way to incoherent, and why uniform motion decays by friction to thermal motion. It should be just as easy to accept that, whatever the manifestations of the dissymmetries identified by the Second Law, they are aspects of dispersal.

As energy collapses into chaos, the events of the world move forward. But in Chapter 2 we saw that change is accompanied by an increase of entropy. Entropy must therefore be a measure of chaos. Moreover, we have seen that the natural tendency of events corresponds to the corruption of the quality of energy. Consequently, quality must reflect the absence of chaos. High-quality energy must be undispersed energy, energy that is highly localized (as in a lump of coal or a nucleus of an atom); it may also be energy that is stored in the coherent motion of atoms (as in the flow of water). We are on the brink of uniting these concepts. We have a picture of what it means for the spring of the world to unwind: now we must relate this picture to the entropy. As we do so, we shall acquire Boltzmann's vision of the nature of change.
4 THE ENUMERATION OF CHAOS

Carved on a tombstone in the central cemetery in Vienna is an equation. It is not only one of the most remarkable formulas of science, but also the ladder we need to climb from the qualitative discussion of the dispersal of energy up to the quantitative. The tombstone marks Boltzmann’s grave. The formula to the left is our ladder and his epitaph.

Boltzmann’s epitaph summarizes most fittingly his work. The letter $S$ denotes the entropy of a system. The letter $k$ denotes a fundamental constant of Nature now known as Boltzmann’s constant (in what follows we do not need its actual value; so we shall pretend it is equal to unity). The letter $W$ is a measure, in a sense that we shall shortly unfold, of the chaos of a system. Here is our first encounter with a formula that has as many implications for the modern world as Einstein’s $E = mc^2$ (the only other equation that people in general seem prepared to know).

Boltzmann’s equation is central to our discussion because it relates entropy to chaos. On its left we have the entropy, the function which entered thermodynamics in the train of the Second Law and which is the classical signpost of spontaneous change. On the right we have a quantity that relates to chaos because it measures the extent to which energy is dispersed in the world; the concept of energy dispersal, as we have just seen, is at the heart of the microscopic mechanism of change. $S$ stands firmly in the world of classical thermodynamics, the world of distillations of experience; $W$ stands squarely in the world of atoms, the world of underlying mechanism. Boltzmann’s tomb is the bridge between the world of appearance and its underworld of atoms.

As Chapter 2 refined the observations discussed in Chapter 1 that gave rise to the perception that energy possesses quality as well as quantity, so this chapter will refine the qualitative discussion of dispersal we met in Chapter 3. Clausius himself saw what we have already seen: he saw the difference between heat and work, understood the intrinsic incoherence of thermal motion, and appreciated what was meant and what was implied by degradation and dispersal of energy. But the world is indebted to Boltzmann for refining that view into an instrument as sharp as a Japanese sword, and showing us how to cut numbers from chaos.
The program of this chapter is to extend and sharpen the blade we have begun to form: we have to enumerate chaos and see numerically, rather than merely intuitively, that natural events represent collapse into chaos and that, in a quantitatively precise sense, events are motivated by corruption.

Boltzmann's Demon

How can we quantify chaos? What is the meaning of \( W \)? We can arrive simultaneously at both answers by considering a special initial case of the Mark I universe and allowing it to run through its subsequent history. The special initial state is shown below: every atom in System 1 is ON; every atom of System 2 is OFF.

The question we now ask is the following: how many ways can the inside of a system be arranged without an external observer being aware that rearrangements have occurred? The answer is what is meant by the quantity \( W \). Notice how this captures what we have earlier called the essential step in going from atoms to systems, an observer's blindness to individuals. Thermodynamics is concerned with only the average behavior of great crowds of atoms, and the precise role being played by each one is irrelevant. If the thermodynamic observer doesn't notice that change is occurring, then the state of the system is regarded as the same: it is only the minutely precise observer who insists on scrutinizing individual atoms who knows that change is actually in progress.

We shall imagine a Demon, a little, insubstantial, neutral, mischievous, and eternally busy thing. I shall call it Boltzmann's Demon*. Its business consists of forever reorganizing. In the universe it simply rearranges ON-ness and OFF-ness. It is the incarnation of the lack of rules that rules the universe. Being infinitely disorganized, all it does is to relocate ONs at random, moving them perpetually but aimlessly.

We, the thermodynamically shortsighted observer, cannot see the Demon. However furiously it reorganizes, so long as it does not change the number of ON atoms in a system (and we note that it can only move ON-ness, not create it), then we cannot see that it is active, or even that it is there. Boltzmann's \( W \), then, is the number of different arrangements his Demon can stumble into without us being aware that changes are afoot. If, however, the Demon does manage to move an ON out into System 2, then we shall know that it has happened: the temperature of System 1 will have dropped, and that of System 2 will have risen. We the shortsighted can see our thermometers.

In the special initial state of the universe that we are considering, the Demon cannot do anything without our noticing. All the atoms are ON in the system, and so ON-ness cannot be shifted around within it. Since there is only one arrangement possible in which all the atoms in System 1 are ON, we conclude that \( W = 1 \). Since the logarithm of unity is zero, Boltzmann's equation gives us the entropy of this state of System 1 as zero. There is zero entropy in this highly localized, tidy collection of energy; so it has perfect quality.

In time, however, the Demon will succeed in moving one ON-ness into the other system (see the figure on the following page). This is the dawn of the Demon's day. Now it can rearrange the ON-nesses within System 1 in many different ways, and we the external observer will be none the wiser. It is quite easy to calculate the new value of \( W \); it is equal to the number of different ways of choosing which atom is to be OFF. There are 100 atoms in System 1, and as the Demon moves 99 ON-nesses around, there are 100 places for the location of the one OFF. That is, \( W = 100 \); this state of the system is one that the Demon can arrange in 100 different ways. Then,

* J. C. Maxwell had a Demon too. Maxwell's Demon, by no means is quite different from Boltzmann's Demon, and the two should not be confused.
One ON-ness has escaped from System 1 into System 2; the resulting OFF in System 1 can be in 100 different places, the single ON in System 2 can be in 1,500 different places.

since the natural logarithm of 100, \( \ln 100 \), is 4.61, Boltzmann's epitaph gives the entropy of this state as 4.61. The entropy of System 1 is greater than before; the system is more chaotic because we do not know the location of just one OFF.

In due course the Demon will succeed in turning another atom OFF in System 1 and transferring its energy to an atom of System 2. Now there are two gaps in the ON-ness of System 1, and the Demon has more scope for its invisible mischief. The number of ways of arranging the 98 ON-nesses it has at its disposal in System 1 is the same as the number of arrangements of the two OFFs it now must have there. One of these OFFs can turn up at any of the 100 sites; the second can turn up at any of the remaining 99 sites (see the figure on the facing page). Therefore the total number of arrangements of ON-nesses that the Demon can succeed in stumbling into is \( 100 \times 99 = 9,900 \). However, some of these arrangements are identical. For instance, the Demon could first turn OFF atom 23 and then turn OFF atom 32, or it could first turn OFF atom 32 and then atom 23. The end result in each case is the same; atoms 23 and 32 are OFF. Therefore we should divide the previous number by 2, because only half the 9,900 arrangements are different. This means that \( W = 4,950 \), and that the Demon has 4,950 different ways of reorganizing System 1 without us knowing that anything is going on. Using Boltzmann's tomb, we find that the entropy of System 1 has risen to \( \ln 4,950 \approx 8.51 \).

We must not forget that the entropy of System 2 is increasing. Initially it was zero, because no atom was ON, and there is then only one arrangement. Then, when the Demon happened to ship out one ON-ness from System 1 to System 2, one atom turned ON. In System 2 there are 1,500 locations for ON, and so the number of undetectable and indistinguishable ways of arriving at this thermodynamic state of System 2 is 1,500; its entropy therefore is \( 1,500 \times 7.31 = 10,965.5 \). If there are two ON-nesses to accommodate one in System 2 in 1,500 locations, the other in any of the remaining 1,499. Again, we must not double-count; so the total number of different arrangements is half of \( 1,500 \times 1,499 \), or 1,124,250. This is the number of different ways in which the thermodynamic state of System 2 can be achieved. The entropy of this state is the logarithm of this number: \( \ln 1,124,250 = 13.93 \). Notice that the entropy of System 2 is increasing more rapidly than the entropy of System 1: because System 2 is larger than System 1, a single ON-ness in System 2 can be located at more sites than in System 1; the Demon has more scope for rearrangement when it has more atoms to turn ON and OFF.

We could continue to calculate the numbers of arrangements that the Demon can explore, and then take logarithms to arrive at the corresponding entropies. Numbers get very large, but the advantage of taking logarithms is that they cut big numbers down to small: logarithms are very lazy.
numbers. (For instance, the natural logarithm of 100 is 4.61; the natural logarithm of Avogadro's number is 54.7, even though the number itself is more than $10^{23}$.) Therefore, although numbers of arrangements may become astronomical, the corresponding entropies remain terrestrial.

The history of the initial state may be pursued into the future using the Entropy program in Appendix 2. The values of the entropy of each system and of the universe (their sum) are shown above. The entropy of System 1 initially rises, because the Demon has more freedom to locate the ONs as soon as gaps are available; but as soon as half the atoms are turned OFF, the entropy begins to fall, because now the Demon is running short of ONs. If all the atoms were to be extinguished, the Demon would be unable to act; so the entropy would again be zero. The entropy of the other system behaves differently: although it is gaining energy, it will never acquire enough to turn one half of its atoms ON (there are only 100 ONs initially, whereas System 2 has 1,500 atoms). Therefore the entropy of System 2 only rises. The entropy of the universe as a whole therefore goes through a maximum.

From the graph we see that the maximum of the universe's entropy occurs when the proportion of atoms ON to OFF in System 1 is the same as that in System 2, that is, when their temperatures are the same. This is exactly what we expect the entropy to signify. We have seen intuitively that energy will disperse, and we know that this dispersal must correspond to the increase of the universe's entropy. Now we have seen that Boltzmann's epitaph captures both wings of description: "energy tends to disperse" is equivalent to saying that "entropy tends to increase."

Notice too how the illustration at the top of the facing page lets us account for the natural direction of energy flow in a temperature gradient. Suppose we have an initial arrangement of the universe in which only one atom of System 1 is ON, and 99 atoms of System 2 are ON. Then we know from our earlier remarks that the temperature of System 1 is lower than that of System 2 (the temperatures are respectively 0.22 and 0.38 if we use the formula given on page 56). The entropy of the universe is therefore at the point marked A in the figure on the left. Intuitively we know what will happen: the energy of System 2 will flow into System 1 until it is uniformly distributed over the entire available universe (see the figure on the next page). This corresponds to each of the 1,600 atoms having an equal likelihood of being ON: since there are 100 ONs overall, at equilibrium we can predict that the chance of any one being ON is 0.0625, 0.0625, whether the atom belongs to System 1 or to System 2. Since there are 100 atoms in System 1, the number of its atoms ON at equilibrium is $100 \times 0.0625 = 6.25$. However, that number must be an integer because atoms are only fully ON or OFF; therefore the number must be fluctuating around 6 and 7; for simplicity we take it to be 6 (or occasionally 7). The other 94 (or 93) ON atoms are therefore all in System 2.

When 6 (or 7) atoms are ON in System 1, the temperature is 0.36 (0.39); when 94 atoms are ON in System 2, its temperature is 0.37 (it is also 0.37 when 93 are on, because in the bigger system the temperature is less sensitive to numbers). These temperatures are virtually the same (the difference arises from the fact that we have rounded 0.25 to 0.5 or 7). Not only are the temperatures the same, but they correspond (as we can see from the figure to the left) to the maximum value of the entropy of the universe, point B, exactly as our earlier discussion requires; the cooling to thermal equilibrium corresponds to an increase toward maximum entropy.
The Demon's Cage

Each successful quantitative step of science brings in its wake new qualitative insight. The progress of science can often be traced to a symbiosis of insight and mathematics: each one eases the other along, and as progress is made so comprehension flourishes. The same is true of the step we have now taken: the step, from the intuitive notion of chaos to its precise formulation in terms of the number of arrangements open to a system but invisible to an external observer.

The new insight obtained from Boltzmann's model concerns the nature of equilibrium. In the model we have been considering, the maximum entropy of the universe occurs when the two systems are at thermal equilibrium. Then there is no net flow of energy from one to the other, and there the two systems will remain forever, except for chance fluctuations that happen, very occasionally, to ripple the evenness of the distribution. At thermal equilibrium the systems appear to be at rest, and net change is quenched. But in fact the Demon is as active as ever. Boltzmann's Demon never dies; it scours furiously and randomly from atom to atom, extinguishing here and igniting there. Thermal equilibrium is an example of dynamic equilibrium, where the underlying motion continues unabated and the externally perceived quiet is an illusion. Almost all the final resting conditions of the processes that we shall consider are dynamic equilibria of this kind, and we shall see many examples of atomic life continuing after the bulk seems dead.

But there is an even more important point. Dynamic equilibrium represents the Demon caught in the cage of its own spinning. Thermal equilibrium, as we have seen, corresponds to the condition of maximum universal entropy. It therefore also corresponds to the thermodynamic (average) state that can be achieved in the maximum number of ways. If we think of the universe as being able to exist with many arrangements of ONs scattered over either system, then different scatterings may correspond to different thermodynamic states; but in general many different scatterings of ONs will correspond to each state. We can then ascribe a probability to each thermodynamic state in terms of the number of ways in which, at a microscopic level, it can be achieved. Then the more ways in which a state can be achieved, the higher its probability, in the sense that a chance scattering of ONs is more likely to land in an arrangement corresponding to a given thermodynamic state if that state can be achieved in many ways. In this sense the uniform distribution (which is also the one that can be achieved in most ways) is the most probable state of the universe. In other words, thermal equilibrium corresponds to the most probable state of the universe.

This conclusion can be expressed in a slightly different way. We allow the Demon perfect freedom to shift and change; therefore, in due course, it runs through all the possible arrangements of 100 ON-nesses (and may enter many arrangements many times). We may have to wait a trillion years, but the time will come when every configuration of the universe will have been achieved. However, almost all the arrangements correspond to a uniform distribution of ON-ness: perhaps for a millisecond in those trillion years the universe will be found with all the atoms of System 1 turned ON, but for most of the time the energy will be almost uniform. This is because there are so many arrangements that correspond to uniformity (but which are imperceptibly different to the onlooker) that the Demon spends most of its time generating them, and for only a miniscule fraction of its time does it happen to achieve others.

This point can be explored by using the Fluctuation program in Appendix 3. Of course, with a universe of only 1,600 atoms and with System 1 being as small as 100 atoms, the chance that significant abnormalities will be stumbled into by the Demon is quite large. Nevertheless, if the program is run, it will be found that substantial fluctuations occur only infrequently, and most of the Demon's labors are imperceptible. As an example of this kind of behavior, the figures on the next two pages show several frames in succession: all of them correspond to having six or so atoms ON in System 1. Even though the atoms that are ON are different in each frame, we of the blunted thermodynamic eye cannot perceive that. We regard the system as being in a steady state: the thermostat remains steady while the Demon deploys.

This feature of change is exceedingly important. There are many states
Some more of the myriad of arrangements of ONs at thermal equilibrium. Most of the time there are 6 or 7 atoms ON in System 1.

of the universe, and the random wandering of the energy permits them all, in principle, to be achieved. A fragment of the universe might begin in a highly improbable state (for example, in the arrangement shown in the top figure on page 71, in which System I is relatively cold). After that we shall see the universe drifting through ever more-probable states. That is the natural direction of spontaneous change. When the universe arrives at a more probable state (that is, one that can be achieved in more ways), it almost certainly does not return to a less probable one, because the likelihood of random jostling taking it there by chance is too remote. The final condition of equilibrium of the universe is then its most probable state. The Demon has spun its own cage; the very chaos with which it acts ensures that it is trapped in the future and cannot return to the past. It could return to the past by unraveling chaos if it acted purposely; but it acts at random, and chaos cannot undo chaos except by chance.

Such are the properties of the model universe. The properties of our actual Universe mirror them precisely, but its energy can be dispersed in so many ways that extraordinary structures may emerge and appear stable as the Universe sinks virtually irreversibly toward equilibrium. However, we have now discovered the essentially statistical way in which systems evolve. We see that the irreversibility of natural change results not from certainty, but from probability: perceived events correspond to the evolution of the Universe through successive states of increasing (and, once attained, overwhelming) probability. In principle, therefore, the Universe has loopholes for miracles.

It would be regarded as a minor miracle, for instance, if a lump of metal were suddenly spontaneously to glow red hot, let alone if water were spontaneously to turn into wine. But the Demon might succeed in bringing about at least the lesser miracle, and could do so by chance. It is conceivable, because the probability is not absolutely zero, that the aimless actions of the Demon could accumulate a great deal of energy in a tiny region of the Universe. But the probability of that happening is negligible, and the probability that the fundamental particles of water might stumble into an arrangement that we would recognize as wine is even more remotely infinitesimal. The loophole exists, but it is almost infinitely small, and the greater probability is that the reports of miracles are exaggerations, falsely reported rumors, hallucinations, deceptions, misunderstandings, or simply tricks. To paraphrase David Hume: it is always more probable that the reporter is a deceiver than that the miracle in fact occurred.

Chaos, Coherence, and Corruption

The relation of the entropy to W as expressed by the Boltzmann equation sharpens the meaning of chaos. We shall do two things with it. First, we shall express more precisely what happens in the course of natural change. Then we shall use it to encompass the disorder in the way that matter is arranged.
Consider what is involved in the chaotic disruption of coherence, as when the ordered motion of a body (see figure on left) gives way to thermal motion (as we discussed for the bouncing ball). The entropy of the initial state of the body is zero, because all the atoms are moving coherently. In terms of the activities of the Demon, there is no way in which it can rearrange the ON-ness, for any change would alter the state of motion of the body, which we would detect. Hence Boltzmann's $W$ is equal to unity, and his equation gives an entropy of zero. The body might be warm, in which case it would possess an entropy, but that would merely add a thermal contribution to the total; for simplicity we shall suppose the temperature to be zero, and therefore that there is no entropy from this source. The table that the body is about to strike is also perfectly cold, or so for simplicity we may suppose.

When the perfectly cold body strikes the perfectly cold table, energy is dissipated into the thermal motion of the atoms of both. The entropy of the table and the body therefore both rise, because now the Demon has ONs to deploy. Overall, therefore, there has been an increase of entropy.

The universe is shifting toward a state of higher probability. Initially there is only one arrangement for the ON-ness of the atoms (and indeed they have to be not merely ON but ON in a definite direction). This coherent motion of correlated excitation would be a very improbable outcome if the Demon were simply handed a bag of ONs and were left to deploy them. On the other hand, each successive bounce leaves the universe in a more probable arrangement, one that the Demon is more likely to achieve. In the end, when the energy is uniformly and incoherently distributed, the universe is in its most probable state, the state in which the Demon can spin arrangements almost forever without detection.

Now we take the last step toward the complete identification of chaos. Suppose that the particles of the universe are free to move, and that they, as well as their energy, can move from place to place, as they could if the universe were a gas. Suppose we prepare an initial state by injecting a puff of gas into one corner of the universe (upper figure on right). We know intuitively what will happen: the cloud of particles will spontaneously spread and in due course fill the container.

This behavior is easy to understand in terms of the onset of chaos. A gas is a cloud of randomly moving particles (the name "gas" is, in fact, derived from the same root as "chaos"). The particles are dashing in all directions, colliding, and bouncing off whatever they strike. The motion and the collisions quickly disperse the cloud, and before long it is uniformly distributed over the available space (lower figure on right). There is now only an extremely remote chance that the particles will ever again simultaneously and spontaneously accumulate back in their original cor-
ner. Of course, we could drive them back into the corner with a piston, but that would involve doing work, and the accumulation would not have been spontaneous.

Clearly, the idea that energy tends to disperse accounts for the change we have just described, for now the ON-ness of the atoms has been physically dispersed as the atoms themselves spread. Each atom carries kinetic energy, and the spreading of the atoms spreads the energy. But in what sense has the entropy increased? We can get the answer from the Boltzmann expression by thinking in terms of the value of W and the activity of the imperceptible Demon.

An initial state of the universe in which all 100 particles of gas lie in the left half of the container.

Suppose the initial cloud occupies one-half of the entire universe, as in the figure above. We know, from experience, that in a final equilibrium state the gas will be spread throughout the universe (as in the figure on the facing page), and therefore occupy twice the original volume. In the initial state the Demon’s domain is only on the left, and then we know that some particle A must be there. In the final state the Demon can deploy the atoms (which, for convenience, we shall regard as all being equally ON) in either half of the universe. Atom A now may be either on the left or on the right. So long as there are compensating shifts of other particles, as the Demon (now disguised as the chance collisions) moves the atoms from place to place, the external observer is unaware that the inner structure of the gas is a tumultuous storm.

The equilibrium state of the gas, where the particles are distributed uniformly. Now any particle is equally likely to be found in the right half or the left half of the container. The entropy of this state is greater than the initial state by 100 ln 2.

For each particle, the number of locations the Demon can move it to is increased by a factor of 2 when the gas is allowed to spread throughout the entire universe. Consider two particles: when the second is also allowed to explore the entire universe, it too has twice as many possible locations as it had at first. Therefore, in a sample of two atoms the number of arrangements corresponding to the same energy increases when the cloud expands by a factor of $2 \times 2 = 2^2$. For three the increase is a factor of $2 \times 2 \times 2 = 2^3$, and so it goes on. For a sample of 100 particles the value of W increases by a factor of $2^{100}$. Therefore the Boltzmann equation tells us that the entropy increases from its original $\ln W$ to $\ln (2^{100} \times W)$. The increase is therefore the difference of these two quantities, $\ln 2^{100}$. This increase is equal to $100 \ln 2$, or 69.3. Hence here also, as we should expect, we have an increase in the entropy of the universe.

The Boltzmann equation therefore captures another aspect of dispersal: the dispersal of the entities that are carrying the energy. In fact his tomb is universal. However energy is dispersed, by spreading from one platform to another, or by the platforms themselves spreading and mingling with other platforms, or by a simple loss of coherence within a sample, it corresponds to the increase of entropy. That is the power of the Boltzmann equation: it enumerates corruption in all its forms.

* We are using the property of logarithms which tells us that $\log a^x = x \log a$. In the next step we use the relation that $\log a^x = \log a$. The rules are true for logarithms to any base.
5 THE POTENCY OF CHAOS

This is the turning point of the fortunes of chaos. Our hero, apparently committed to a life of dissipation, degeneration, and general corruption, is about to make good.

On the one hand, we have the world of phenomena: the immediate world of appearance and process. This is symbolized by the steam engine. On the other, we have the world of underlying mechanism. This is symbolized by the atom.

Reflection on experiences with the steam engine identified a dissymmetry in the workings of Nature, which, we found, could be encapsulated in the remark that the entropy of the universe always increases in any natural change. Entropy, we saw, was related to the value of Heat supplied/Temperature. We also saw an economic consequence of the dissymmetry: there is an intrinsic inefficiency, a tax to pay, when heat is converted into work. This inefficiency is governed by the temperatures involved in the operation of an engine.

Reflection on the microscopic world of atoms showed that we should expect natural processes to be those in which there is a dispersal of energy. We have refined the meaning of "dispersal," and have seen that it signifies the spreading of energy, either by the motion of what carries it or by its transfer from one carrier to another. We have also seen that dispersal signifies a loss of coherence in the manner in which energy is stored. We have claimed that all the processes of the world are aspects of this general dispersal, and that spontaneous processes are the manifestation of the purposeless, underlying spreading that chance brings about and that lack of regulation allows.

The bridge between the two worlds is the epitaph on Boltzmann's tombstone (see page 65). It relates the entropy, as encountered in the world of experience, to a measure of dispersal, which we can interpret in terms of events in the microscopic world. The Universe, we have seen, is ineluctably drifting through states of ever-increasing probability. Once any new state has been attained (by any natural action), the Universe is locked out of the past, for any turning back is too improbable to be significant.
CHAPTER 5

That is the general background to the events that surround us and take place within us. But Nature has an extraordinary way of slipping into chaos, and sometimes (often, in fact) does so unevenly. The world does not degenerate monotonously. Here and there a constructive act may effloresce, as when a building or an opinion is formed. The descent into universal chaos is not uniform, but more like the choppy surface of rapids. In a local arena there may be an abatement of chaos, but it is an abatement driven by the generation of even more chaos elsewhere.

We now need to unravel the network of connections that Nature drives as it sinks into chaos. We shall begin by returning to the Carnot cycle, newly equipped with our insight into the purposeless behavior of atoms and energy, and see how the corruption of the quality of the energy in the world may bring about local abatements of chaos. Then we shall explore the structural potency of chaos.

Carnot under the Microscope

We can build a simple model of the Carnot engine using the Mark II version of the universe (below). The Mark II universe, remember, is like the Mark I, but the surroundings of the system of interest are infinite: the hot source is an inexhaustible supply of energy, and the cold sink is an insatiable absorber of energy. The indicator diagram for the Carnot cycle we described in Chapter 1 is reproduced above, right. What we now have to establish is how the random dispersal of energy succeeds in producing coherent motion: we have to establish at a microscopic level how heat is converted into work.

At A, at the start of the cycle, the working gas is at the temperature of the hot source. That is, the ratio of the number of ON atoms and OFF atoms is the same in both. (We are taking the simplistic view that the energy needed to turn an atom ON is the same in the surroundings as in the working substance.) From now on we shall say simply, "The ON:OFF ratio is the same." The atoms of the gas are free to move and collide with anything that happens to lie in their path.

All the walls except one are rigidly fixed in place. The exception is the piston. The crucial feature of the engine is that it possesses at least one wall that can move in response to the impacts it receives. Here is an essential asymmetry of the engine: it possesses a directional response to the impacts it receives. The face of the piston is, in effect, a screen: it picks out and responds to the motion of particles that happen to be traveling perpendicular to it; and it rejects (by not responding to) components of motion that happen to be parallel to it. Engines, in effect, select certain motions of the particles within them. The directionality of the movement of an actual piston in an engine is a consequence of this asymmetry. Our exploitation of heat to achieve work is based on the discovery that the randomness of thermal motion can be screened and sorted by asymmetry of response. The random thermal motion of the particles of gas is transformed into coherent motion of the particles that constitute the piston (and then of whatever the piston is rigidly attached to). As a result, some of the particles are switched OFF, because they have jostled away their motion (see the top figure on the next page). However, since the gas remains in contact with the hot source as the piston moves back, and since energy continues to
The microscopic events taking place in the isothermal power stroke from A to B. The thermal motion of the ON atoms is given up as the coherent motion of the particles of the piston, but the energy is restored because of the thermal contact between the gas and hot source. Energy jostles in, and maintains the temperature (the ON:OFF ratio) of the gas atoms.

jostle in its normal purposeless way, the ratio of numbers ON and OFF actually remains the same. The A to B leg of the cycle is therefore the consequence of purposeless wandering, with the asymmetry of the environment extracting coherence from random motion.

At B the thermal contact with the environment is broken. The piston continues to respond to impacts, and goes on being driven out, but no more energy can jostle in from the hot source (below). In this adiabatic step, therefore, atoms are turned OFF as they give up their energy to the piston. The ON:OFF ratio falls, and with it falls the temperature.

The events during the adiabatic power stroke from B to C. Although the thermal motion continues to be converted into the coherent motion of the particles of the piston, the thermal insulation of the gas means that the ON:OFF is not restored. The number of atoms ON decreases, so the temperature falls. (In the engines, recall, the number of atoms in the cylinder remains constant; this feature is misrepresented by the model.)

The crank has now turned so far that the piston begins to reverse and compress the gas. On a microscopic scale, this means that the coherent motion of the particles of the piston is stimulating the motion of the gas particles: although the stimulated motion is briefly coherent, it rapidly degrades to thermal motion. In other words, the piston turns atoms ON. Since the gas is now in thermal contact with the cold sink, the excess energy jostles away, and the proportion ON (and hence the temperature) remains constant.

At C the turning of the crank reverses the direction of motion of the piston, and thermal contact is established with the cold sink (above). Now the coherent motion of the incoming piston stimulates the particles to move more rapidly as they collide with it (just as ping-pong balls go faster after being hit by the paddle; compression is just a vast, simultaneous game of ping-pong). Thus work is being done on the gas, because energy is being transferred to it by the coherent motion of the particles of the piston. This coherent motion is picked up by the particles of gas. However, the particles collide among themselves so rapidly that in fractions of a second the motion has become incoherent. Although work is being done, the coherence of the motion is dissipated so quickly that it results in incoherence. The gas, however, although it is increasingly turned ON, does not get hotter; the jostling of the atoms among themselves and with the walls ensures that the gas remains at the same temperature as the cold sink with which it is now in contact.

At D the thermal contact with the sink is broken, and the compression becomes adiabatic. The particles of the piston continue to stimulate the motion of the particles of the gas, and more and more of these turn ON (see figure on the next page). Now they cannot jostle their energy to the surroundings; so the work done by the incoming piston raises the temperature of the gas. This brings us to A, and the cycle is complete.

In the course of completing the cycle, more disorder than order has been created. The coherent raising of the weight to which the piston is attached is a process perfectly free of entropy production (so long as it is quasistatic). We draw energy from the hot source. That reduces its disorder, for with fewer atoms ON, the Demon has less scope for rearrange-
In the final, adiabatic step from A to B, the incoming power continues to stimulate atoms to turn ON. The energy cannot escape because of the thermal insulation, so the number ON (and with it the temperature) rises.

In the adiabatic step from B to C, this number begins to fall, but the energy is not used to do work. Instead, it is stored in the form of thermal energy, which increases the temperature. The total energy in the system remains constant, but the energy distribution changes.

In the adiabatic step from C to D, the temperature decreases, but the energy is not released. Instead, it is stored in the form of kinetic energy, which decreases as the number of ON atoms decreases. The total energy in the system remains constant, but the energy distribution changes again.

In the adiabatic step from D to A, the temperature increases again, but the energy is not released. Instead, it is stored in the form of potential energy, which increases as the number of ON atoms increases. The total energy in the system remains constant, but the energy distribution changes once more.

This cycle can be repeated indefinitely, with the energy being stored and released in different forms at each step. The total energy in the system remains constant, but the energy distribution changes at each step.

The cycle is not perfect, however. Some energy is lost to the surroundings, and some energy is lost as heat. This means that the cycle cannot be repeated indefinitely without some loss of efficiency. However, the cycle can still be useful for converting energy from one form to another.

Stirling's Engine

The Carnot engine is an abstract design. One reason why it cannot be used to build a practical machine is apparent from the illustration on page 10: the area bounded by the cycle is very small. Although the cycle is efficient (if gone through quasistatically), each rotation of the crank delivers very little work. In the remainder of this chapter, we shall examine some of the cycles that are used commercially: we shall see that each is driven by the generation of chaos, even though ostensibly each is driven by the consumption of fuel. Our trucks, automobiles, and jet airliners are all impelled by corruption.

Robert Stirling was a minister of the church and active during the opening years of the nineteenth century, when people were being killed or maimed by explosions that resulted from the use of increasingly higher steam pressure in engines. The ambitions of the engineers outstripped the capabilities of the metallurgists, as they sought to confine high pressure within the inadequate steels of the time. As befitted his calling, he grieved over such personal tragedy, and was to devise an engine that would work...