EINSTEIN AND THE QUANTUM

THE QUEST OF THE VALIANT SWABIAN

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CHAPTER 4

TWO PILLARS OF WISDOM

> The man loved mysterious Nature as a lover loves his distant beloved. In his day there did not exist the dull specialization that stares with self-conceit through horn-rimmed glasses and destroys poetry.
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> —**ALBERT EINSTEIN, ON MICHAEL FARADAY**

"About Max Planck's studies on radiation, misgivings of a fundamental nature have arisen in my mind, so that I am reading his article with mixed feelings." So Einstein wrote to his Dolly from Milan in April of 1901, a scant four months after Planck's "act of desperation" in Berlin had saved his own reputation but failed to alert the physics community to the storm ahead. In the same letter Einstein ruefully admits, "soon I will have honored all physicists from the North Sea to the southern tip of Italy with my [job inquiry]." Emboldened by his first published article, which had appeared in the prestigious journal *Annalen Der Physik*, Einstein had sent a slew of postcards requesting an assistant's position to the well-known physicists and chemists of Europe. None of these missives bore fruit, and as far as we know few of them were even graced with a reply. Although Einstein was convinced that Weber was behind the rejections, Einstein's indifferent final academic record and his failure to receive the pro forma job offer from the Poly would likely have been enough.

Despite these disappointments he was scraping together a living through part-time jobs and private lessons and forging ahead with his independent thinking about the current state of theoretical physics. For much of this time he would be separated from his fiancée, but writing to her frequently. In his very next letter to Maric he continues discussing Planck: "Maybe his newest theory is more general. I intend to have a go at it." A little later in the letter he comments, "I have also somewhat changed my idea about the nature of the latent heat in solids, because my views on the nature of radiation have again sunk back into the sea of haziness. Perhaps the future will bring something more sensible." His last words were prescient; his views on radiation would emerge from haziness to enlarge the Planck radiation theory in a revolutionary manner, while the latent (or specific) heat of solids, a seemingly mundane topic, would provide Planck's theory with the radical physical interpretation that it currently lacked. But before this could occur, Einstein needed to plumb deeply into thermodynamics, Planck's specialty, and the newer atomistic discipline of statistical mechanics, which attempted to explain and extend the laws of thermodynamics. His main scientific motivation at the time was not to unravel the puzzles of relative motion. Einstein's famous insight, that resolving these puzzles would require a major reshaping of our conceptions of time and space, would not occur to him for four more years. Rather, his primary scientific focus from his student days was "to find facts which would attest to the existence of atoms of a definite size." Proving the existence of atoms and understanding the physical laws governing their behavior was the original quest of the Valiant Swabian.

The atomic world was the frontier of physics at the beginning of the twentieth century. The disciplines of what is now called classical physics had all developed without a need to delve too deeply into the question of the nature of the microscopic constituents of matter. That situation had now changed. If physics was going to progress, it would be essential to understand the fundamental origin of electromagnetic phenomena, of heat flow, of the properties of solids (e.g., electrical conductivity, thermal conduction and insulation, transparency, hardness), and the physical laws leading to chemical reactions. The answers to these questions would only be found by understanding the makeup of the atom and the physical interactions between atoms and molecules.

Modern physics had begun with the work of Sir Isaac Newton in the second half of the seventeenth century. He introduced a new paradigm for the motion of objects (masses) in space: first by the bold assertion that the natural state of motion of a solid body is to move at a constant speed in a straight line (Newton's First Law), and then by the statement that the state of motion changes in a predictable manner when "forces" are acting on the body (Newton's Second Law). If one knew the force and mass of the body, the Second Law would determine the instantaneous acceleration of the mass, a, via the relation $F/m = a$. What it meant to speak of the *instantaneous* rate of change of any quantity wasn't (and isn't) obvious, but Newton cleared this up by means of a mathematical innovation, the invention of calculus. From this point forward, mechanics came to mean the study of the motion of masses under the influence of forces described by elaborations of Newton's Second Law, which could now be written as a "differential equation" using calculus.

For this law to be useful, scientists would need to have a mathematical representation of the forces in nature, the F on the left-hand side of $F = ma$. The forces of nature cannot be deduced; they can only be hypothesized (okay, guessed) and tested for whether their consequences make sense and agree with experimental measurements. No amount of mathematical legerdemain can get around that. Newton's Second Law was an empty tautology unless one had an independent mathematical expression for the forces that mattered in a given situation.

Newton gained eternal fame by divining the big one, the one we all know from infancy: the force of gravity. His universal law of gravitation stated that two masses are attracted to each other along the line between their centers, and the strength of that attraction is proportional to the product of their masses and inversely proportional to the square of the distance between them. Of course this attraction is very weak between normal-size masses like two people, but between the earth and a person or the earth and the sun it is a big deal. From this law of gravitation and his Second Law, Newton was able to calculate all kinds of solid-body motion: the orbits of the planets in the solar system, the relation between the moon and tides, the trajectories of cannonballs. Thus Newton had published the first major section of the

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"book of Nature," which was, Galileo famously declared, "written in the language of mathematics."

Along with the stunning mathematical insights of Newton and their vast practical applications came an ontology, a view of what the fundamental categories of nature were, and how events in the world were related. As Einstein put it in his autobiographical notes, "In the beginning—if such a thing existed—God created Newton's laws of motion together with the necessary masses and forces. That is all. Anything further is the result of suitable mathematical methods through deduction. What the nineteenth century achieved on this basis . . . must arouse the admiration of any receptive man . . . we must not therefore be surprised that . . . all the physicists of the last century saw in classical mechanics a firm and empirical basis for all . . . of natural science."

At the core of the Newtonian view of nature was the concept of rigid determinism, majestically expressed by the Marquis de Laplace:

> We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at any given moment knew all of the forces that animate nature and the mutual positions of the beings that compose it, if this intellect were vast enough to submit these data to analysis, could condense into a single formula the movements of the greatest bodies of the universe and that of the lightest atom; for such an intellect nothing could be uncertain and the future just like the past would be present before its eyes.

This Marquis Pierre Simon de Laplace was one of the great masters of classical mechanics in the nineteenth century and became known as the "French Newton." He was willing to literally put his neck on the line for his natural philosophy. When he presented his five-volume study of celestial mechanics to Napoleon, he was greeted with the intimidating question: "Monsieur Laplace, they tell me you have written this large book on the system of the universe and have never even mentioned its Creator." Laplace, normally quite politic in his dealings with influential men, in this case drew himself up and replied bluntly, "I have no need of that hypothesis."

While the relation between mass and the force of gravity was the only fundamental law discovered by Newton, he and other physicists knew that there must be other forces with associated laws, for example, the pressure exerted by a gas (pressure is force per unit area), which surely must have a microscopic origin. Near the end of the eighteenth century Charles Augustin de Coulomb, using a sensitive instrument known as the torsion balance, definitively measured another type of force, also of invisible origin: the electrical force. Coulomb and others determined that, in addition to mass, there is another important property of matter, electrical charge, and that two charged bodies exert forces on each other in a manner similar to the way gravity works in Newton's Second Law, that is, proportional to the product of their charges and inversely proportional to the square of the distance between them. However, there is a major difference between this electrostatic force and gravity; charges come in two types, positive and negative. Opposite charges attract each other, but like charges repel. Matter is usually electrically neutral (that is, made up of an equal number of positive and negative charges) or very nearly neutral, so two chunks of matter don't usually exert much long-range electrical force on each another. Therefore, despite the fact that the electrical force is much stronger than the gravitational force (when appropriately compared), it doesn't have the same kind of macroscopic effects as gravity.

Early in the nineteenth century it became clear that the story was even more complicated. Moving charges (i.e., electrical currents) create yet another force, known to the ancients but not understood as related to electricity: magnetism. Primarily through the work of the English experimental physicist Michael Faraday, it became clear that electricity and magnetism were intimately related because, for example, magnetic fields could be used to create electrical currents. Exploiting this principle, discovered in 1831 and now known as Faraday's law, Faraday was able to build the first electrical generator (he had earlier made the first functioning electric motor). Faraday's discovery would lead to an expansion of the classical ontology of physics, because it implied that electrical charges and currents gave rise to unseen electric and magnetic *fields*, which permeated space and were not associated with matter at all but rather represented a *potential* to exert a force on charged matter. These were the "unseen forces" that moved the compass needle, which had fascinated Einstein as a child. Besides masses, forces, and charges, there were now fields as well.

Faraday had risen from the status of a lowly bookbinder's apprentice to become Fullerian Professor of Chemistry at the Royal Institution (during his life he rejected a knighthood and twice declined the presidency of the Royal Society). When asked by the four-time prime minister William Gladstone the value of electricity, he is said to have quipped,[1] "One day sir, you may tax it." He had little formal mathematical education and showed by experiment that his ideas were correct but did not formulate them into a rigorous theory.

That task was left to the Scottish physicist/mathematician James Clerk Maxwell. Maxwell was a deeply religious man, related to minor nobility, who showed an Einsteinian fascination with natural phenomena from a young age. As early as age three he would wander around the family estate asking how things worked, or as he put it, "What's the go o' that?" He is widely regarded as the third-greatest physicist of all time, after Newton and Einstein, although he is surely much less known to the public. He wrote his first important scientific paper at the age of sixteen and attended Cambridge University, where he excelled and became a Fellow shortly after graduation. One of his contemporaries wrote of him, "He was the one acknowledged genius . . . it was certain that he would be one of that small but sacred band to whom it would be given to enlarge the bounds of human knowledge." At the age of twenty-three Maxwell expressed his philosophy of science in terms that prefigure similar sentiments of both Planck and Einstein:

> Happy is the man who can recognize in the work of today a connected portion of the work of life, and an embodiment of the work of Eternity. The foundations of his confidence are unchangeable, for he has been made

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[1] This wonderful incident may well be apocryphal, as there is no contemporaneous account of it.

> a partaker of Infinity. He strenuously works out his daily enterprises, because the present is given to him for a possession.

Maxwell had a full beard and a certain reserved presence that was hard to warm up to (very unlike Einstein, the mensch); however, he was a loyal friend and an almost saintly husband—in all, a man of character and integrity. Despite his diffidence, he possessed a rapier-like wit, which he would only occasionally display, as in the following. In his forties, having "retired" to his Scottish country estate for health and personal reasons, he was convinced to return to England to head the new Cavendish Laboratory at Cambridge; he did a superb job and became an important administrative figure in British science. In this capacity he was asked to explain to Queen Victoria the importance of creating a very high vacuum. He described the encounter thus:

> I was sent for to London to be ready to explain to the Queen why Otto von Guerike devoted himself to the discovery of nothing, and to show her the two hemispheres in which he kept it . . . and how after 200 years W. Crookes has come much nearer to nothing and has sealed it up in a glass globe for public inspection. Her majesty however let us off very easily and did not make much ado about nothing, as she had much heavy work cut out for her all the rest of the day.

The young Maxwell came to know the much older Faraday personally as well as through his work and realized that his experimental discoveries, which Faraday had framed qualitatively, could be cast into a set of equations that describe all electromagnetic phenomena in four compact formulas, now universally known as Maxwell's equations. Like Newton's Second Law these are four differential equations, not describing masses and forces but rather electrical fields, magnetic fields, electrical charges and currents. If Maxwell had used only Faraday's law and the previously known laws of electrostatics and magnetism, he would have found similar equations but with a disturbing asymmetry between the role of the electric and magnetic fields. Maxwell decided in 1861 that these two fields were different expressions of the same unified force, and had the

FIGURE 4.1. James Clerk Maxwell at roughly the age at which he proposed the fundamental laws of classical electromagnetism. Courtesy of the Master and Fellows of Trinity College Cambridge.

brilliant insight to add a new term to one of the equations describing the magnetic field, which had the effect of making the full set of equations perfectly symmetric in regions of space where there were no electrical charges or currents (as in vacuum). Thus he essentially added a major clause to the laws of electromagnetism. The new term gave rise to new effects, called "displacement currents," which were verified experimentally. They also made the equations structurally perfect. Boltzmann, quoting Goethe, said of Maxwell's equations, "was it God that wrote those lines?"

Having added his new contribution to the electromagnetic laws, Maxwell made a historic discovery: electric and magnetic fields could propagate through the vacuum in the form of a wave that carried energy and could exert both electric and magnetic forces. In physics the term *wave* refers to a disturbance in a medium (e.g., water or air) that oscillates in time and typically is extended, at any single instant, over a large region of space. In this case the strength of the disturbance is measured by the strength of the electric field, so that if an electric charge sat at one point in space the electric field would push the charge alternately up and then down, like a rubber ball bobbing on surface waves propagating through water. Moreover, if you moved along with the wave, like a surfer, the field would always push you in one direction, just as the surfboard stays at the leading edge of a water wave (for a while).

Maxwell showed that the distance between crests of the electromagnetic waves could be made arbitrarily large or small; that is, any wavelength was possible. Thus he discovered what we now call the electromagnetic spectrum, extending, for example, from radio waves having a wavelength of a meter, to thermal radiation (as we saw earlier) at ten millionths of a meter, visible light at half a millionth of a meter, and on to x-rays at ten billionths of a meter. This was a spectacular finding; but the epiphany, the earthshaking revelation, was the speed of the waves: all of them traveled at the same speed, the speed of light! Suddenly disparate phenomena involving man-made electrical devices, natural electric and magnetic phenomena, color, and vision were unified into one phenomenon, the propagation of electromagnetic waves at 186,000 miles per second.

The beauty and significance of this discovery has awed physicists ever since. One of the greatest modern theoretical physicists, Richard Feynman, wrote of this event: "From the long view of the history of mankind . . . the most significant event of the nineteenth century will be judged as Maxwell's discovery of the laws of electrodynamics. The American Civil War will pale into provincial insignificance in comparison with this important scientific event of the same decade." Maxwell himself, with typical understatement, wrote to a friend in 1865, "I have also a paper afloat, with an electromagnetic theory of light, which, until I am convinced of the contrary, I hold to be great guns."

Maxwell would go on to make other major contributions to physics, specifically with his statistical theory of gases, which will be of great relevance below, but he was not recognized as a transcendent figure during his lifetime. He died of abdominal cancer in 1879 at the age of forty-eight, still at the peak of his scientific powers. While in hindsight we view Maxwell as poorly rewarded in his time for his genius and service to society (he was never knighted, for example), Maxwell did not see it that way. On his deathbed he told his doctor, "I have been thinking how very gently I have always been dealt with. I have never had a violent shove in my life. The only desire which I can have is, like David, to serve my generation by the will of God and then fall asleep."

Maxwell's achievement particularly captivated Einstein. Maxwell, Faraday, and Newton were the three physicists whose picture he had on the wall in his study later in life. Of Maxwell he wrote, "[the purely

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mechanical world picture was upset by] the great revolution forever linked with the names of Faraday, Maxwell and Hertz. The lion's share of this revolution was Maxwell's . . . since Maxwell's time physical reality has been thought of as represented by continuous fields. . . . this change in the conception of reality is the most profound and fruitful that physics has experienced since the time of Newton." Elsewhere he said, "Imagine his feelings when the differential equations he had formulated proved to him that electromagnetic fields spread in the form of . . . waves and with the speed of light"; and, "to few men in the world has such an experience been vouchsafed."

Maxwell had completed the second pillar of classical physics, what we now call classical electrodynamics, to go along with the first pillar, classical mechanics. But neither his nor Newton's equations in themselves answered the fundamental question: what is the universe made of? One knew that there were masses and charges and forces and fields, but what were the building blocks of the everyday world? The enormous challenge was to extend these physical laws down to this conjectured "atomic" scale. Were there new, microscale forces not detectable at everyday dimensions? Did Newton's and Maxwell's laws still hold there? Were atoms little billiard balls with mass and electrical charge obeying classical mechanics and electrodynamics? Were there atoms at all, or were they just "theoretical constructs," as many physicists and chemists maintained until the end of the nineteenth century?

At the time of Maxwell there was no way to probe the internal structure of atoms or molecules directly. As Maxwell put it, "No one has ever seen or handled a single molecule. Molecular science therefore . . . cannot be subjected to direct experiment." However physicists, led by Maxwell and Boltzmann, were beginning to use the atomic concept to explain in great depth the macroscopic behavior of gases. In doing so they were inferring properties of atoms and their interactions. This was the work that Einstein never forgave Herr Weber, his erstwhile mentor, for ignoring. It is here that Einstein first put his shoulder to the wheel.

CHAPTER 5

THE PERFECT INSTRUMENTS OF THE CREATOR

"The Boltzmann is magnificent," Einstein wrote to Maric in September of 1900. "I am firmly convinced that the principles of his theory are right, . . . that in the case of gases we are really dealing with discrete particles of definite finite size which are moving according to certain conditions . . . the hypothetical forces between molecules are not an essential component of the theory, as the whole energy is kinetic. This is a step forward in the dynamical explanation of physical phenomena." Einstein was reading Boltzmann's *Lectures on the Theory of Gases.* The Viennese physicist Ludwig Boltzmann and Maxwell had developed a theory of gases in the 1860s with much the same content, but with the difference that Boltzmann wrote long, difficult-to-decode treatises, while Maxwell's work was much more succinct. Maxwell commented on this drily: "By the study of Boltzmann I have been unable to understand him. He was unable to understand me on account of my shortness, and his length was and is an equal stumbling block to me." Einstein, despite the enthusiasm he expressed to his fiancée in 1900, was later to warn students, "Boltzmann . . . is not easy reading. There are very many great physicists who do not understand it." It is likely that Einstein had no access to Maxwell's work on gases in 1900, and as he did not read English until much later in life, he would not have been able to benefit from it anyway (in contrast, Maxwell's electrodynamics was available to Einstein in German textbooks).

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Maxwell beautifully described the scientific advance he had made in atomic theory in an address to the Royal Society in 1873 titled, simply, "Molecules."

> An atom is a body which cannot be cut in two. A molecule is the smallest possible portion of a particular substance. The mind of man has perplexed itself with many hard questions. . . . [Among them] do atoms exist, or is matter infinitely divisible? . . .
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> According to Democritus and the atomic school, we must answer in the negative. After a certain number of sub-divisions, [a piece of matter] would be divided into a number of parts each of which is incapable of further subdivision. We should thus, in imagination, arrive at the atom, which, as its name literally signifies, cannot be cut in two. This is the atomic doctrine of Democritus, Epicurus, and Lucretius, and, I may add, of your lecturer.

Maxwell goes on to describe how chemists had already learned that the smallest amount of water is a molecule made up of two "molecules" of hydrogen and one "molecule" of oxygen (here he has decided, somewhat confusingly, to use molecule to refer to both atoms and molecules). Then he arrives at his current research.

> Our business this evening is to describe some researches in molecular science, and in particular to place before you any definite information which has been obtained respecting the molecules themselves. The old atomic theory, as described by Lucretius and revived in modern times, asserts that the molecules of all bodies are in motion, even when the body itself appears to be at rest. . . . In liquids and gases, . . . the molecules are not confined within any definite limits, but work their way through the whole mass, even when that mass is not disturbed by any visible motion. . . . Now the recent progress of molecular science began with the study of the mechanical effect of the impact of these moving molecules when they strike against any solid body. Of course these flying molecules must beat against whatever is placed among them, and the constant succession of these strokes is, according to our theory, the sole cause of what is called the pressure of air and other gases.

This simple picture, that gas pressure arises from the collisions of enormous numbers of molecules with the walls of the container, along with simple ideas of classical mechanics, allows Maxwell to derive Boyle's law, that the pressure of the gas is proportional to its density. It also allows him to understand the observation that the ratio of volumes of any two gases depends only on the ratio of temperatures of the gases. The relation of temperature to volume of a gas is critical: in this view absolute temperature (what we now call the kelvin scale) is related to molecular motion and is proportional to the average of the square of the molecular velocity in a gas. Since the energy of motion for any mass, called kinetic energy, is just one-half its mass times the square of the velocity, this also means that for a gas its energy is just proportional to temperature. As Einstein had noted in his letter to Maric, in the Maxwell-Boltzmann theory, the entire energy of a gas is the kinetic energy of moving molecules. This principle of the Maxwell-Boltzmann theory, that the energy of each molecule is proportional to the temperature, applies even in the solid state, in which the molecules vibrate back and forth around fixed positions instead of moving freely throughout the substance. This property of the theory would perplex Einstein later, when he was trying to make sense of Planck's radiation law.

"The most important consequence which flows from [our theory]," Maxwell continues, "is that a cubic centimetre of every gas at standard temperature and pressure contains the same number of molecules." This fact about gases was conjectured by the Italian scientist Amadeo Avogadro in 1811. In 1865 Josef Loschmidt, a professor in Vienna and later a colleague of Boltzmann, had estimated this actual number, which is very large: 2.6×10^{19}, or roughly five billion *squared*. (This "Loschmidt number" is closely related to Avogadro's number, which is the number of molecules in a mole of any gas—both Einstein and Planck were very interested in accurately determining these numbers). With all this information about gas properties, it was possible for Maxwell to determine the average velocity of a molecule in air. He found it to be roughly one thousand miles per hour. He described the implications most picturesquely:

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> If all these molecules were flying in the same direction, they would constitute a wind blowing at the rate of seventeen miles a minute, and the only wind which approaches this velocity is that which proceeds from the mouth of a cannon. How, then, are you and I able to stand here? Only because the molecules happen to be flying in different directions, so that those which strike against our backs enable us to support the storm which is beating against our faces. Indeed, if this molecular bombardment were to cease, even for an instant, our veins would swell, our breath would leave us, and we should, literally, expire. . . . If we wish to form a mental representation of what is going on among the molecules in calm air, we cannot do better than observe a swarm of bees, when every individual bee is flying furiously, first in one direction, and then in another, while the swarm as a whole . . . remains at rest.

Maxwell goes on to describe how his own experiments and others have determined that the molecules in a gas are continually colliding with one another, moving only about ten times their diameter before changing direction again through a collision, leading to a kind of random motion called diffusion. Because of this constant changing of direction, the actual distance moved from the starting point during a given time is much less than if the molecule were moving in a straight line. This explained why, when Maxwell took the lid off a vial of ammonia in the lecture, its characteristic odor was not immediately detected in the far reaches of the lecture hall. The same kind of diffusion occurs in liquids such as water, but much more slowly. Maxwell then throws off a poetic but profound comment: "Lucretius . . . tells us to look at a sunbeam shining through a darkened room . . . and to observe the motes which chase each other in all directions. . . . This motion of the visible motes . . . is but a result of the far more complicated motion of the invisible atoms which knock the motes about." Exactly this process occurs to small particles suspended in a liquid but visible under a microscope, so-called Brownian motion. In one of his four masterpieces of 1905 Einstein would actually take the suggestion of Lucretius and Maxwell seriously and, by careful analysis, turn this into a precise method for determining Avogadro's number! Experiments by the

French physicist Jean Perrin would confirm Einstein's predictions and determine that number very precisely; as a result Perrin received the Nobel Prize for Physics in 1926, long after his work had permanently put to rest doubts about the existence of atoms.

The kind of complex, essentially random motion characteristic of gas molecules gave rise to a new way of doing physics, described by Maxwell in the same lecture. "The modern atomists have therefore adopted a method which I believe new in the department of mathematical physics, though it has long been in use in the section of statistics." Thus was born the discipline of *statistical mechanics*. Maxwell could only assume that the invisible molecules obeyed Newtonian mechanics; he had no reason to doubt this. But in describing what would happen in a gas, he realized that one must inevitably encounter the weak point in Laplace's grandiose dictum. Laplace had imagined an intellect that "at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed." Maxwell realized that getting all the necessary information and using it to predict the future was an absurd proposition. "The equations of dynamics completely express the laws of the historical [Laplacian] method as applied to matter, but the application of these equations implies a perfect knowledge of all the data . . . but the smallest portion of matter which we can subject to experiment consists of millions of molecules, not one of which becomes individually sensible to us . . . so that we are obliged to abandon the historical method and to adopt the statistical method of dealing with a large group of molecules." Maxwell's point is that for all practical purposes one doesn't want to know what each molecule is doing anyway; for example, to find the pressure exerted by a gas one needs only to know the *average* number of molecules hitting the wall of a container per second, and how much momentum (mass times velocity) they transfer to the wall.

This was the key insight of Maxwell and Boltzmann: to predict the physical properties of a large aggregation of molecules, one needed only to find their average behavior, assuming they were behaving as randomly as allowed by the laws of physics. Calculating these properties was relatively easy for a gas, where most of the time the molecules are not in close contact; for liquids and solids it was much harder and in certain cases still challenges the physicists of the twenty-first century. Tied up with this insight was a new understanding of the laws of thermodynamics. The First Law says that heat is a form of energy, and that the total energy (heat plus mechanical) always stays the same (is "conserved") even when one form is being changed into the other. For example, when a car is moving at 60 miles per hour, it has a lot of mechanical energy, specifically kinetic energy, $\frac{1}{2}mv^2$, where m is the mass of the car and v is its speed (60 mph in this case). When you slam on the brakes, that kinetic energy doesn't disappear; it is turned into heat in your brakes and tires, due to friction. From the point of view of statistical mechanics, that heat is just mechanical energy transmitted to the molecules of the road and tires, distributed in some complicated and apparently random manner among them. So heat is just random, microscopic mechanical energy, stored in various forms in the atoms and molecules of gases, liquids, and solids.

This view sheds light on the Second Law, which states that disorder always increases and is measured by a quantity called entropy. This law now can be interpreted as saying that in any process where something changes (e.g., the car coming to a stop), you can never perfectly "reorganize" all the energy that goes into the random motion of molecules. It is always too hard to retrieve all of it in a useful form. Before the car stopped, all its molecules (in addition to some random motion due to its non-zero temperature) were moving together in the same direction at 60 mph, providing a kinetic energy that could be used to do useful work, such as dragging a heavy object against friction. As the car stops, that energy is transformed into the less usable form of heat. It is not that we can't turn heat back into usable energy (e.g., use it to get the car moving again); it is just that we can't do it perfectly. We could run some water over the hot brake discs of our stopped car, which could generate steam, which could turn a turbine, and, presto, we would get back some useful mechanical energy. This of course is not the best-designed heat engine one could imagine. But the Second Law says that no matter how carefully or cleverly you design an engine to turn heat into useful mechanical energy, you will always find that you have to put more heat energy in than you get back.

To make this all precise and tractable in a mathematical theory, the German physicist Rudolph Clausius, while a professor at our familiar Zurich Poly in 1865, introduced the notion of entropy, which is a measure of how much the microscopic disorder increases in every process involving heat exchange. The word *entropy* was chosen from the Greek word for "transformation," and indeed Clausius was guided by just the picture we have been painting: heat is the internal energy of atoms or molecules, which can be partially but never fully transformed to usable energy. Now, with their new statistical mechanics, Maxwell and Boltzmann were trying to make this idea of the internal energy of a trillion trillion rocking and rolling molecules precise, and in so doing come to understand entropy and the laws of thermodynamics on the basis of atomic theory. This program was so controversial that even by the end of the century, thirty years later, Planck, the thermodynamicist par excellence, was reluctant to adopt it. It was only his quantum conundrum that forced him to overcome his scruples, as we will see.

The key point is that the statistical mechanics of Maxwell and Boltzmann was still *Newtonian mechanics*, just applied to a system so complicated that one imagines it behaving like a massive game of chance, in which each molecular collision with a wall or with another molecule is like a coin being tossed (heads you go to the right, tails you go to the left). The *worldview* is the same as that of Newton and Laplace; only the method is different. Maxwell, had he lived another two decades, might have begun to recognize the leaks springing in this optimistic vessel, since the basic inconsistency in this view appeared at the intersection of his two great inventions, the theory of electromagnetic radiation and the statistical theory of matter. However, that was not to be; he would pass away a mere five years after his spectacular lecture on molecular science, having spent those final years occupied by his administrative duties. At the end of that same lecture, having anticipated the next twenty-five years of physical theory, the devout Maxwell makes one of the great historical appeals for intelligent design:

> Natural causes, as we know, are at work, which tend to modify, if they do not at length destroy, all the arrangements and dimensions of the earth

> and the whole solar system. But . . . the molecules out of which these systems are built . . . remain unbroken and unworn.
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> They continue this day as they were created, perfect in number and measure and weight, and from the ineffaceable characters impressed on them we may learn that those aspirations after accuracy in measurement, truth in statement, and justice in action, which we reckon among our noblest attributes as men, are ours because they are essential constituents of the image of Him Who in the beginning created, not only the heaven and the earth, but the materials of which heaven and earth consist.

The next century would demonstrate in many ways, culminating in the awesome demonstration of August 1945, that atoms are not as indestructible as Maxwell had supposed. And Einstein would be the first to understand, through his most famous equation, $E = mc^2$, just how much energy would be released when the perfect instruments of the Creator were disassembled.

CHAPTER 6

MORE HEAT THAN LIGHT

"I have again made the acquaintance of a sorry example of that species—one of the leading physicists of Germany. To two pertinent objections which I raised about one of his theories and which demonstrate a direct defect in his conclusions, he responds by pointing out that another (infallible) colleague of his shares his opinion. I will shortly give that man a kick up the backside with a hefty publication. Authority befuddled is the greatest enemy of truth."

Such was the feisty mood of Einstein as he wrote in July of 1901 to an old friend, Jost Winteler. The object of his ire was Paul Drude, theorist and chief editor of *Annalen der Physik*, the most prestigious physics journal in the world at that time. Drude himself was the author of a well-respected text on optics and Maxwell's equations (in fact it was Drude who introduced the universal symbol *c* for the speed of light in vacuum). The "infallible" colleague mentioned by Einstein was none other than Ludwig Boltzmann. Einstein, characteristically, seemed oblivious to the potential consequences of offending such prominent scientists, one of whom was editor of the journal to which he would submit all his original research papers for the next six years.

Einstein wrote those lines from the small city of Winterthur, about twenty miles from Zurich, where he had a two-month position teaching physics and mathematics at the Technical College while the regular instructor was performing his military service. The teaching load was quite heavy, thirty hours a week, but, undeterred, he reassured Mileva that "the Valiant Swabian is not afraid." In fact he found that he enjoyed the teaching much more than he had expected, and despite the busy schedule he managed time to study research questions, such as

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Drude's new "electron theory of metals." It was only four years earlier, in 1897, that the English physicist J. J. Thomson had confirmed the existence of electrons, negatively charged particles much lighter than the hydrogen atom itself, and he hypothesized that electrons were constituents of atoms. By 1899 Thomson had shown that electrons could be pulled off atoms (a process we now call "ionization") and hence that the atom was in this sense divisible. This represented the first crack to appear in the indestructible atoms of Maxwell.

Drude's theory was based on a guess about the atomic properties of metals. He hypothesized (correctly) that, in a metal such as copper, one of the electrons in each atom was free to move. While the atoms themselves remained fixed in a solid regular crystalline array, these free electrons formed a gas of charged particles that could move easily through the solid, allowing it to conduct electricity and heat efficiently. Drude's hypothesis was that many of the important properties of metals arose from this gas of electrons, and he thus could use the kinetic theory of Maxwell and Boltzmann to calculate those properties. This was an important step forward, and some of Drude's conclusions were based on such general considerations that they remain true and are used in our modern (quantum) theory of metals. Other conclusions he drew from his theory relied on Newtonian mechanics and are now known to be false. Einstein's letter to Drude, pointing out his "errors," and Drude's reply are lost, so nothing is known about the validity of Einstein's objections. What is known is that around this time Einstein began his own reworking of the basic principles of statistical mechanics.

Einstein's very first published work on atomic theory (the one he sent along with his job inquiries) was based on a naive hypothesis about molecular forces: that they behaved similarly to gravity in that they depended only on the distance between molecules, and on the type of molecules involved. He wrote about this work to his former classmate Grossmann in April of 1901: "As for science, I have a few splendid ideas. . . . I am now convinced that my theory of atomic attraction forces can also be extended to gases. . . . That will also bring the problem of the inner kinship between molecular forces and Newtonian action-at-a-distance forces much nearer to its solution." Einstein's simple attraction hypothesis was wrong, and despite his initial enthusiasm he abandoned it after using it in two articles for *Annalen der Physik*, which he later referred to as "my worthless first two papers." These works did emphasize that at the time there was no real understanding among physicists about the origin of molecular forces. After the modern atomic theory was established, it became clear that all the atomic forces important for chemistry or solid-state physics ultimately arise from electromagnetic forces; there *are* no special new molecular forces.[1] However, how atoms *behave* under the influence of these forces is quite different from what was expected, because they obey a new mechanics (quantum mechanics) and not the classical mechanics of Newton. (In addition, there are new forces within the atomic nucleus, hinted at by the phenomenon of radioactivity, which had just been discovered, but these forces are generally not important for chemistry or solid-state physics.) Einstein praised Boltzmann's statistical theory of gases precisely because it *didn't* rely much on the unknown molecular forces, and after his first immature efforts he decided to pursue the path of statistical mechanics into the atomic realm.

At the end of 1901 Einstein received "A letter from Marcelius [Marcel Grossmann] . . . a very kind letter" telling him that the patent office position would soon be advertised and that he would definitely get it. "In two months time we would then find ourselves in splendid circumstances and our struggle would be over," he wrote to Maric, but, he hastened to add, their bohemian lifestyle would not change "We shall remain students [horribile dictu] as long as we live, and not give a damn about the world." One more professional disappointment remained. In November 1901 Einstein submitted a PhD thesis on the kinetic theory of gases to Professor Alfred Kleiner at the University of Zurich (the Poly was not yet able to grant PhD degrees, although with Weber in charge it is not likely that Einstein would have tried

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[1] There are forces inside the atomic nucleus that were unknown at that time, now called, unimaginatively, the "strong" and "weak" nuclear forces. At that time the existence of the nucleus was itself unknown.

that route anyway). Only indirect information survives about what transpired, but Einstein withdrew the thesis early in 1902, apparently at Kleiner's suggestion, "out of consideration for [Kleiner's] colleague Ludwig Boltzmann," who, despite Einstein's admiration for his work, had been "sharply criticized" on certain points.

By February of 1902 Einstein had relocated to Bern, a picturesque Swiss city on the river Aare. His job at the patent office would not start for five months, and he remained without visible means of support, so he literally hung out his shingle.

Private Lessons in
Mathematics and Physics
for students and pupils
given most thoroughly by
Albert Einstein, holder of the fed.
polyt. teacher's diploma
Gerechtigkeitgasse 32, 1st floor
Trial Lessons Free

"The situation with the private lessons isn't bad at all. I have already found two gentlemen, an engineer & an architect & more in prospect," Einstein wrote to Maric shortly after arrival. His letter was apparently a bit *too* cheerful, as he soon received a reply from his fiancée, which is lost, but the content of which is clear from Einstein's rapid follow-up: "It is true . . . that it is very nice here. But I would rather be with you in some backwater than without you in Bern." Actually, although Einstein painted a rosy picture of his life in Bern, an old family friend who visited him there described his condition as "testifying to great poverty . . . [living in] a small, poorly furnished room." Strikingly, Einstein never complains in his letters about material conditions, making only occasional humorous allusions to this "annoying business of starving."

In Bern Einstein quickly gathered around him a lively circle of friends with shared intellectual interests, several of whom would become lifelong companions. By the end of June 1902 he had taken up his post at the patent office as an expert third class (the lowest rank), and his immediate financial woes were ended. In October of that year he obtained grudging permission from his parents (at his father's deathbed) to marry Mileva, and on January 6, 1903, with no family present, only two friends, the couple were married with complete lack of ceremony at the Bern registry office. Typically, Einstein had trouble getting into their new apartment that night, as he had forgotten the key. Mileva had gone through many tribulations to get to this point, and it seems that after failing twice to get her teacher's degree from the Poly, she had now given up her own scientific ambitions. Einstein reports to his friend Michele Besso that she takes good care of him and he "leads a very pleasant, cozy life" with her; in the same letter he tells Besso that he has just sent off his second paper on statistical mechanics, pronouncing the paper "perfectly clear and simple, so that I am quite satisfied with it."

The main point of Einstein's first two papers on statistical mechanics was to frame all the statistical relations that ultimately underlie the First and Second Laws of thermodynamics in a very general way, no longer referring specifically to gases and collisions in gases, as was done by Maxwell and Boltzmann. Thermodynamics is supposed to apply to everything that stores energy and can absorb or give off heat, which is essentially everything: liquids, solids, machines, . . . you name it. The Second Law of thermodynamics implies that no engine can change heat into useful work with perfect efficiency. Stated more picturesquely, it is impossible to make a perpetual-motion machine, a machine that, once it gets started, will go forever in a repeated cycle without needing fuel. Einstein, in his new job at the patent office, was regularly coming across proposed "inventions" that, upon closer inspection, were physically impossible because they violated this principle. The generality of the laws of thermodynamics must have been very much on his mind.

And so he wrote two papers that assume almost nothing about the nature of molecular forces, or the macroscale nature (e.g., gas, solid, etc.) of the thermodynamic system being considered, and that lead to several equivalent forms of the Second Law. The papers make only one assumption, an assumption so subtle that it had been the cause of debate since the time of Maxwell. Einstein appears to have been unaware of this raging debate and does not emphasize this assumption (to be discussed later) or comment on it in any detail. However, the mathematical results of these papers and the formal framework he introduces are quite important, and would alone have made his name known a century later, except for some bad luck.

Independently, and earlier, Josiah Willard Gibbs at Yale University had established exactly the same principles ("the resemblance is downright startling," Max Born later commented) and applied them very powerfully to chemical problems. Gibbs, the son of an eminent theologian and scion of an old New England family, received in 1863 the first PhD in engineering granted in the United States. He briefly studied in Europe and became acquainted with the nascent German school of thermodynamics, begun with Clausius and continuing in Einstein's day with Planck. Very reminiscent of Maxwell in his breadth of interests, Gibbs would make enormous contributions as a physicist, chemist, and mathematician until his death in 1903; he is arguably the greatest American-born scientist of all time. In fact Maxwell himself was so impressed with a clever geometric method devised by Gibbs to determine chemical stability that he made a plaster model illustrating the idea with his own hands and sent it to Gibbs.

Gibbs introduced the concept of "free energy," which dominates modern statistical mechanics and is often denoted by the symbol G in honor of Gibbs; this is just one of *twelve* important scientific contributions bearing his name to this day. His work was initially slow in becoming known in Europe, but just as Einstein was beginning his own statistical studies, Gibbs's monumental treatise, *Elementary Principles of Statistical Mechanics*, was published, and he was awarded the Copley Medal of the Royal Society of London. (Before the Nobel prizes, which were first awarded in 1901, this was the most prestigious international science award of the day.)

Gibbs's contributions predated and overwhelmed those of Einstein, and Einstein would later comment in print that had he known of Gibbs's work earlier, he would "not have published those papers at all, but confined myself to a the treatment of some few points [that were distinct]." Einstein's admiration for Gibbs remained so great throughout his life that when, a year before his death in 1955, he was asked who were the most powerful thinkers he had known, he replied: "[Hendrik] Lorentz,[2] I never met Willard Gibbs; perhaps, had I done so, I might have placed him besides Lorentz." So already, before his twenty-fifth birthday, Einstein had established himself as a deep thinker, on par with the great leaders of his era; unfortunately no scientist of any influence seems to have noticed this at the time. Moreover he was not advancing his career aspirations by telling the leading physicists in Germany of the errors they had made in their earlier work. He would need to devise new theories, which made specific experimental predictions, to get the world's attention. These would not be long in coming, and when they did come, the free-spirited bohemian outsider would soar above even the great men—Maxwell, Gibbs, and Lorentz—whom he so admired.

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[2] Hendrik Lorentz, a Dutch physicist, was widely regarded as the most eminent theorist of the generation preceding Einstein's; he will play an important role in our story below.