JIM BAGGOTT
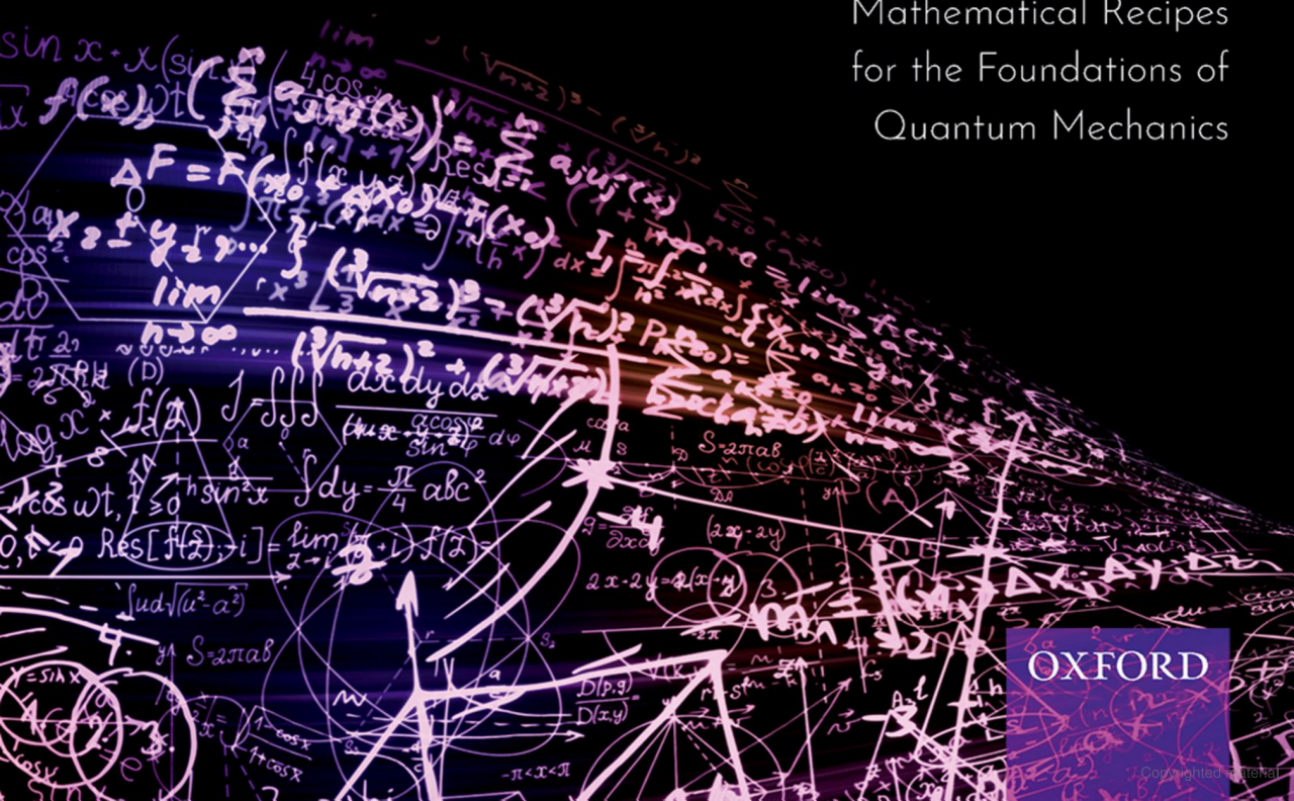
THE QUANTUM
COOKBOOK

Mathematical Recipes
for the Foundations of
Quantum Mechanics

OXFORD

The Quantum Cookbook

Mathematical Recipes for the Foundations of Quantum Mechanics

Jim Baggott

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Jim Baggott is an award-winning science writer. A former academic scientist, he now works as an independent business consultant but maintains a broad interest in science, philosophy, and history, and continues to write on these subjects in his spare time. His books have been widely acclaimed and include the following:

Quantum Reality: *The Quest for the Real Meaning of Quantum Mechanics - A Game of Theories* (2020)

Quantum Space: *Loop Quantum Gravity and the Search for the Structure of Space, Time, and the Universe* (2018)

Mass: *The Quest to Understand Matter from Greek Atoms to Quantum Fields* (2017)

Origins: *The Scientific Story of Creation* (2015)

Farewell to Reality: *How Fairy-tale Physics Betrays the Search for Scientific Truth* (2013)

Higgs: *The Invention and Discovery of the 'God Particle'* (2012)

The Quantum Story: *A History in 40 Moments* (2011, re-issued in 2015)

Atomic: *The First War of Physics and the Secret History of the Atom Bomb 1939–49* (2009, re-issued in 2015), shortlisted for the Duke of Westminster Medal for Military Literature, 2010

A Beginner's Guide to Reality (2005)

Beyond Measure: *Modern Physics, Philosophy and the Meaning of Quantum Theory* (2004)

Perfect Symmetry: *The Accidental Discovery of Buckminsterfullerene* (1994)

The Meaning of Quantum Theory: *A Guide for Students of Chemistry and Physics* (1992)

Prologue

What's Wrong with This Picture?

The Description of Nature at the End of the Nineteenth Century

Anyone already familiar with some of the more bizarre implications of quantum mechanics—its phantoms of probability; particles that are waves and waves that are particles; cats that are at once both alive and dead; its uncertainty, non-locality, and seemingly 'spooky' goings-on—might look back rather wistfully on the structure of classical mechanics. We might be tempted to think that classical mechanics offers a much more appealing or comforting description of nature, one that is unambiguous, definite, and certain.

There is a persistent myth that, towards the end of the nineteenth century, such was the appeal of the classical structure that it seemed to physicists that all the most pressing problems had now been solved. In a lecture delivered to the British Association for the Advancement of Science in 1900, the great physicist Lord Kelvin (William Thomson) is supposed to have declared: 'There is nothing new to be discovered in physics now. All that remains is more and more precise measurement.'[1]

Except there is no evidence that Kelvin ever said this.[2] It's true that in *Light Waves and Their Uses*, a book based on a series of lectures delivered in 1899 to the Lowell Institute in Boston, Massachusetts, American physicist Albert Michelson wrote:[3]

> Many other instances might be cited, but these will suffice to justify the statement that 'our future discoveries must be looked for in the sixth place of decimals.' It follows that every means which facilitates accuracy in measurement is a possible factor in a future discovery.

It is perhaps not surprising that Michelson would want to extol the virtues of just the kind of precise measurement on which he'd built an international reputation. But in April 1900, Kelvin was warning that all was not well. A storm was gathering in the dynamical theory of heat and light.[4] We now know that the classical structure breaks down in the microscopic realm of atoms and subatomic particles, and Isaac Newton's laws of motion can't handle objects moving at or near light speed. However, within its domain of applicability, classical mechanics is surely free of mystery and much less prone to endless bickering about what it's all supposed to mean?

Except that it isn't, really.

Make no mistake, despite its intuitive appeal, classical mechanics is just as fraught with conceptual difficulties and problems of interpretation as its quantum replacement. The problems just happen to be rather less obvious, and so more easily overlooked (or, quite frankly, ignored). Quantum mechanics was born not only from the failure wrought by trying to extend classical physical principles into the microscopic world of atoms and molecules, but also from the failure of some of its most familiar and cherished concepts. To set the scene and prepare us for what follows, I thought it might be worth highlighting some of the worst offenders.

The Interpretation of Space and Time

The classical system of physics that Newton had helped to construct, by 'standing on the shoulders of giants',[5] consists of three laws of motion and a law of universal gravitation. The *Mathematical Principles of Natural Philosophy*, first published in 1687, uses these laws to bring together aspects of the terrestrial physics of everyday objects and the 'celestial' mechanics of planetary motion, in what was nothing less than a monumental synthesis, fully deserving of its exalted status in science history. So closely did the resulting description agree with and explain observation and experiment that there could be little doubting its essential 'truth'. By the end of the nineteenth century it had stood, unrivalled, for more than two hundred years.

Unrivalled, but by no means unquestioned. Newton's mechanics might be intuitive but it demands a number of fairly substantial conceptual or philosophical trade-offs. Perhaps the most fundamental is that Newton's physics is assumed to take place in an *absolute* space and time. This is a problem because, if it existed, an absolute space would form a curious kind of container, presumably of infinite dimensions, within which some sort of mysterious cosmic metronome marks absolute time. Actions impress forces on matter and things happen *within* the container and all motion is then referred to a fixed frame, thereby making all motion absolute.

If we could take all the matter out of Newton's universe, then we would be obliged to presume that the empty container would remain, and the metronome would continue to tick. The existence of such a container implies a vantage point from which it would be possible to look down on the entire material universe, a 'God's-eye view' of all creation.

But a moment's reflection tells us that, despite superficial appearances, we only ever perceive objects to be moving towards or away from each other, changing their *relative* positions. This is relative motion, occurring in a space and time that are in principle defined only by the relationships between the objects themselves. If the motion is uniform, then there is in principle *no* observation we can make that will tell us if this object is moving relative to that object, or the other way around. In the *Mathematical Principles*, Newton acknowledged this in what he called our 'vulgar' experience.

If we can never perceive motion in an absolute space and time then we arguably have no good reason to accept that these exist. And if there is no absolute coordinate system of the universe; no absolute or ultimate inertial frame of reference against which all motion can be measured, then there can be no such thing as absolute motion. Newton's

arch-rival, German philosopher Gottfried Wilhelm Leibniz, argued: 'the fiction of a finite material universe, the whole of which moves about in an infinite empty space, cannot be admitted. It is altogether unreasonable and impracticable.'[6] Now, any concept that is not accessible to observation or experiment in principle, a concept for which we can gather no empirical evidence, is typically considered to be *metaphysical* (meaning literally 'beyond physics').

Why, then, did Newton insist on a system of absolute space and time, one that we can never directly experience and which is therefore entirely metaphysical? Because by making this metaphysical *pre-commitment* he found that he could formulate some very highly successful laws of motion. Success breeds a certain degree of comfort, and a willingness to suspend disbelief in the grand but sometimes rather questionable foundations on which theoretical descriptions are constructed.

Classical Mechanics and the Concept of Force

Classical mechanics is the physics of the ordinary. Suppose we apply a force F for a short time interval, dt, to an object that is stationary or moving with constant velocity, v, in a straight line. In the *Mathematical Principles*, Newton explains that the force is simply an 'action', exerted or impressed upon the object, which effects a change in its linear momentum (p, given by the object's mass m multiplied by v), by an amount dp. If we assume that mass is an intrinsic property of the object and does not change with time or with the application of the force, then dp is then simply the mass multiplied by the change in velocity: $dp = mdv$.

Applying the force may change the magnitude of the velocity (up or down) and/or it may change the direction in which the object is moving. Newton's second law of motion is then expressed as $Fdt = dp$ ($= mdv$). This equation may not look very familiar, but we can take a further step. Dividing both sides by dt gives

$$F = \frac{dp}{dt}. \tag{P.1}$$

Logically, the greater the applied force, the greater the rate of change of linear momentum with time. But, as we've seen, $dp/dt = mdv/dt$. Obviously, dv/dt is the rate of change of velocity with time, or the object's *acceleration*, usually given the symbol a. Hence Newton's second law can be restated as the much more familiar

$$F = ma. \tag{P.2}$$

Force equals inertial mass times acceleration, and we think of inertial mass as the measure of an object's *resistance* to acceleration under an applied force. This is a statement of Newton's second law *equation of motion*.

Though famous, this result actually does not appear in the *Mathematical Principles*, despite the fact that Newton must have been aware of this particular formulation, which

features in German mathematician Jakob Hermann's treatise *Phoronomia*, published in 1716.* It is sometimes referred to as the 'Euler formulation', after the eighteenth-century Swiss mathematician Leonhard Euler.

Newton's version of classical mechanics is expressed in terms of forces which result from the application of various mechanical 'actions'. Whilst it is certainly true to say that the notion of mechanical force still has much relevance today, the attentions of eighteenth- and nineteenth-century physicists switched from force to *energy* as the more fundamental concept. My foot connects with a stone, this action impressing a force on the stone. But a better way of thinking about this is to see the action as transferring energy to the stone.

Like force, the concept of energy also has its roots in seventeenth-century mechanical philosophy. Leibniz wrote about *vis viva*, a 'living force' expressed as mv^2, and he speculated that this might be a *conserved* quantity, meaning that it can only be transferred between objects or transformed from one form to another—it can't be created or destroyed. The term 'energy' was first introduced in the early nineteenth century and it gradually became clear that kinetic energy—the energy of motion—is not in itself conserved. It was important to recognize that a system might also possess *potential* energy by virtue of its physical characteristics and situation. It was then possible to formulate a law of conservation of the *total* energy—kinetic plus potential—largely through the efforts of physicists concerned with the principles of thermodynamics, which we will go on to examine later in this Prologue.

If we denote the kinetic energy as T and the potential energy as V, then the total energy is simply $T + V$. The kinetic energy T is given by

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}. \tag{P.3}$$

It's helpful to understand how this relates to Newton's force, F. Differentiating (P.3) with respect to time gives

$$\frac{dT}{dt} = \frac{1}{2}m\frac{d\left(v^2\right)}{dt} = \frac{1}{2}m\left(v\frac{dv}{dt} + v\frac{dv}{dt}\right) = mv\frac{dv}{dt} = mva. \tag{P.4}$$

In (P.4) we have assumed the mass m to be independent of time and we have applied the product rule $d(uv)/dx = v\left(du/dx\right) + u\left(dv/dx\right)$ to the evaluation of $d\left(v^2\right)/dt$. We can now make use of the second law $F = ma$ and the chain rule

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* Newton published a third edition of the *Mathematical Principles* in 1726 and, if he had been so minded, could have incorporated this version of the second law.

$$\frac{dT}{dt} = Fv \quad \text{and so} \quad dT = Fvdt = F\frac{dx}{dt}dt = Fdx. \tag{P.5}$$

Integrating then allows us to express the kinetic energy in terms of force as follows:

$$T = \int Fdx. \tag{P.6}$$

We can now put Newton's conception of force on a much firmer basis. We *define* the potential energy V as

$$V = -\int Fdx. \tag{P.7}$$

This shift in emphasis from force to energy in the eighteenth and nineteenth centuries meant that it made more sense to define the secondary property of force in terms of the primary property of potential energy:

$$F = -\frac{dV}{dx}. \tag{P.8}$$

Equations (P.7) and (P.8) make perfect sense. Lifting a heavy weight from its initial position on the floor to shoulder height involves the application of a force which changes the potential energy of the weight. The force applied is negative (as its acts *against* gravity), and transfers energy from the gravitational field into the potential energy of the weight. Letting go of the weight exposes it to the force of gravity, converting the gravitational potential energy it contains into kinetic energy, and it falls back to its initial position on the floor. The force is directed in such a way as to reduce the potential energy—hence the negative sign in (P.7)—driving the system 'downhill'. And the 'steeper' the shape of the potential energy curve (the faster the potential energy changes with position), the greater the resulting force, (P.8).

Setting up the relationship between force and potential energy in this way means that in a closed system which cannot exchange energy with the outside world the rate of change of total energy with time balances to zero—energy can be moved back and forth between potential and kinetic forms but the *total energy is conserved*:

$$\frac{dT}{dt} + \frac{dV}{dt} = mva + \frac{dV}{dx}\frac{dx}{dt} = mva + v\frac{dV}{dx} = v\left(ma + \frac{dV}{dx}\right) = v\,(ma - F). \tag{P.9}$$

We can see from this that the time derivatives of the expressions for kinetic and potential energy sum to zero—the total energy doesn't change with time.

This shift of emphasis led to a substantial and profound reformulation of classical mechanics, first by Italian mathematician and astronomer Joseph-Louis Lagrange (in 1764) and subsequently by Irish physicist William Rowan Hamilton (in 1835). This wasn't simply about recasting Newton's laws in terms of energy. Hamilton in particular

greatly elaborated and expanded the classical structure and the result, called *Hamiltonian mechanics*, extended the number of mechanical situations to which the theory could be applied.

Newton's equation of motion $F = ma$ is formulated in terms of position coordinates (such as Cartesian coordinates x, y, z) and time. This is fine in principle for very simple systems involving at most one or two objects, but it quickly becomes problematic for systems involving large numbers of objects. To define the physical 'state' of a system consisting of, say, N objects, such that we can predict how the system will evolve in time, we would need to specify the position *and* the velocity of *each* of the N objects in three-dimensional space, at specific moments in time. It's not enough just to specify the positions—Newton's second law applies to objects that are already in a state of rest or uniform motion, so to predict what happens next we also need to know how fast and in which directions the objects are moving as the force is applied. In other words we need a total of $6N$ coordinates *for each object*.

We can think of the motion of the system as a 'trajectory' in an abstract $6N$-dimensional *configuration space*. Instead of positions and velocities, Hamilton's reformulation makes use of the positions of the objects and their *momenta*. If we keep things simple by restricting ourselves to a single object with inertial mass m moving along a single position coordinate x, then these *canonical coordinates* are (x, p), where p is again the object's linear momentum. Hamilton's choice defines what would subsequently become known as *phase space*.

The motion of the object is then represented by the *trajectory of a point in the phase space coordinates*. This gives us an advantage in more complex systems because instead of specifying the initial positions and velocities of all the objects in a $6N$-dimensional configuration space, in Hamiltonian mechanics we just need to specify the system's initial position in phase space. It then becomes possible to predict the future time evolution of the system from any starting point on its phase space diagram.

As we will draw on many of these concepts in what follows, it's worth taking the time here for a very brief and somewhat superficial look at Hamiltonian mechanics. The *Hamiltonian* of a classical system is simply the total energy, E, and is defined as

$$H\,(= E) = T + V. \tag{P.10}$$

In Hamiltonian mechanics we're obviously interested to know the behaviour of the Hamiltonian H with respect to the canonical coordinates, which in a single dimension are given by (x, p). This behaviour is summarized in Hamilton's equations of motion:

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} \quad \text{and} \quad \frac{dx}{dt} = \frac{\partial H}{\partial p}. \tag{P.11}$$

These equations may appear somewhat unfamiliar, but the second establishes a fairly straightforward connection between momentum and velocity. Remember, we assume

that the potential energy V is independent of p, and from (P.3) we know that $T = p^2/2m$:

$$\frac{\partial H}{\partial p} = \frac{\partial T}{\partial p} = \frac{\partial}{\partial p}\left(\frac{p^2}{2m}\right) = \frac{p}{m} = v = \frac{dx}{dt}. \tag{P.12}$$

And the first is simply a restatement of Newton's second law:

$$-\frac{\partial H}{\partial x} = -\frac{\partial V}{\partial x} = F = \frac{dp}{dt}\,(= ma). \tag{P.13}$$

It's worth noting in passing that we've traded Newton's single equation of motion, which is a *second-order* differential equation (remember, $a = d^2x/dt^2$), for Hamilton's two *first-order* partial differential equations, (P.11).

We can get some sense for how this works by considering a simple example. In one-dimensional simple harmonic motion (such as a low-amplitude pendulum or an object suspended on a spring), an object of mass m oscillates back and forth with an angular frequency ω under the action of a 'restoring' force $F = -m\omega^2 x$. The Hamiltonian for this system is, therefore,

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{P.14}$$

(remember, $V = -\int F dx$), and Hamilton's equations of motion are

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} = -m\omega^2 x \quad \text{and} \quad \frac{dx}{dt} = \frac{\partial H}{\partial p} = \frac{p}{m}. \tag{P.15}$$

If we define the initial position (x_0) to be the origin at time $t = 0$ (i.e. $x_0 = 0$), then the solutions of these equations have the particularly simple form

$$p = p_0 \cos \omega t \quad \text{and} \quad x = \frac{p_0}{m\omega} \sin \omega t, \tag{P.16}$$

where p_0 is the initial momentum. In a phase space with canonical coordinates (x, p), the motion describes an elliptical trajectory:

$$\frac{x^2}{(p_0/m\omega)^2} + \frac{p^2}{p_0^2} = 1. \tag{P.17}$$

Switching to a phase space description allows us to represent the mechanics in terms of the single trajectory of a point in a multidimensional space, summarizing the motion of the *entire system*, not the individual objects. This was a generalization discovered by French mathematician Henri Poincaré in 1888, from his study of the infamous

three-body problem (and which also led him to appreciate the sensitivity of dynamical systems to initial conditions, later to become an obsession of chaos theory).

A year later, Poincaré noted a rather curious phenomenon. In an ideal mechanical system with a finite upper bound on the volume of available phase space (one in which no objects can escape the system and in which energy is conserved), within a sufficiently long, but finite, time the phase space trajectory will return to its starting point.* This is called *Poincaré recurrence*. No matter how many objects are involved, if the dynamics unfold from some starting configuration and we have sufficient patience, the system *will* return to this configuration.

The Troublesome Concept of Mass

The development of our understanding of potential energy in the nineteenth century allowed us to put Newton's concept of force on a much firmer basis, as we've seen. There would appear to be no reason to question our understanding of any of the other concepts which appear in Hamilton's equations. We haven't forgotten the problems of absolute space and time but we surely know what we mean when we talk about acceleration, momentum, and mass.

But what, precisely, *is* inertial mass? Newton provides a handy definition very early in the *Mathematical Principles*:[7]

> *The quantity of matter is the measure of the same, arising from its density and bulk conjunctly . . .*
> It is this that I mean hereafter everywhere under the name body or mass. And the same is known by the weight of each body; for it is proportional to the weight, as I have found by experiments on pendulums, very accurately made, which shall be shewn hereafter.

If we interpret Newton's use of the term 'bulk' to mean volume, then the mass of an object is simply its density multiplied by its volume. It doesn't take long to figure out that this definition is entirely circular, as Austrian physicist Ernst Mach pointed out many years later:[8]

> With regard to the concept of "mass", it is to be observed that the formulation of Newton, which defines mass to be the quantity of matter of a body as measured by the product of its volume and density, is unfortunate. As we can only define density as the mass of a unit of volume, the circle is manifest.

We have to face up to the rather unwelcome conclusion that in classical mechanics we don't really know what inertial mass is.

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* Poincaré's theorem also requires that phase volume is conserved as the system evolves, which is true for all Hamiltonian systems by virtue of Joseph Liouville's 1838 theorem.

The Force of Gravity

In Newton's law of universal gravitation, two objects with masses m_1 and m_2 experience a force of gravity that is proportional to the product of their masses (are these the same as inertial mass?) and inversely proportional to the square of the distance between them, r, or $F = Gm_1 m_2/r^2$, where G is Newton's gravitational constant.

This was another great success, but it also came with another hefty price tag. Although the symbol F might be the same, Newton's force of gravity is distinctly different from the kinds of forces involved in his laws of motion. The latter forces are *impressed*; they are caused by actions such as kicking, shoving, pulling, or whirling. They require physical contact between the object at rest or moving uniformly and whatever it is we are doing to change the object's motion. Newton's gravity works very differently. It is presumed to pass instantaneously between the objects that exert it, through some kind of curious action at a distance. It was not at all clear how this was supposed to work. Leibniz was again dismissive: 'This, in effect, is going back to qualities which are occult or, what is more, inexplicable.'[9]

Newton himself had nothing to offer. In a general discussion (called a 'general scholium'), which he added to the 1713 second edition of the *Mathematical Principles*, he wrote:[10]

> Hitherto we have explain'd the phænomena of the heavens and of our sea, by the power of Gravity, but have not yet assign'd the cause of this power... I have not been able to discover the cause of those properties of gravity from phænomena, and I frame no hypotheses.

Light Waves and the Ether

Newton sought to extend the scope of his mechanics to include light, and in his treatise *Opticks*, first published in 1704, he concluded that light is essentially 'atomic' in nature, consisting of tiny particles, or corpuscles. Two of his contemporaries, English natural philosopher and experimentalist Robert Hooke and Dutch physicist Christiaan Huygens, had argued compellingly in favour of a wave theory of light, and Newton's incendiary disputes with Hooke led him to postpone publication of *Opticks* until after Hooke's death in March 1703. Such was Newton's standing and authority that the corpuscular theory held sway for more than a hundred years.

But in a series of papers read to the Royal Society of London between 1801 and 1803, nearly eighty years after Newton's death, an English medical doctor (and part-time physicist) called Thomas Young revived the wave theory as the only logical explanation for the phenomena of light diffraction and interference. In one experiment, commonly attributed to Young (although historians are divided on whether he actually performed it), he showed that when passed through two narrow, closely spaced holes or slits, light produces a pattern of bright and dark fringes. These are readily explained in terms of a wave theory of light in which the peaks and troughs of the light waves from the two

slits start out in phase, spread out beyond, and overlap. Where a peak of one wave is coincident with a peak of another, the two waves add and reinforce to produce constructive interference, giving rise to a bright fringe. Where a peak of one wave is coincident with a trough of another, the two waves cancel to produce destructive interference, giving a dark fringe.

Today this logic seems inescapable, but Young's conclusions were roundly criticized, with some condemning his explanation as 'destitute of every species of merit'.[11] Nevertheless, as the nineteenth century progressed, the wave theory gained a slow, if somewhat grudging, acceptance. Then, as is so often the case in science, perhaps the most compelling arguments in favour of the wave theory emerged from a seemingly unrelated discipline.

The intimate connection between the phenomena of electricity and magnetism was established over a long period of study in the nineteenth century, most notably through the extraordinary experimental work of Michael Faraday at London's Royal Institution. Drawing on analogies with fluid mechanics, over a ten-year period from 1855 Scottish physicist James Clerk Maxwell developed a theory of *electromagnetic* fields whose properties are described by a set of complex differential equations. These equations can be manipulated to give expressions for the space and time dependences of the electric field E and magnetic field B in a vacuum, as follows (again simplified to one dimension):

$$\frac{\partial^2 \boldsymbol{E}}{\partial x^2} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \quad \text{and} \quad \frac{\partial^2 \boldsymbol{B}}{\partial x^2} = \varepsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{B}}{\partial t^2}. \tag{P.18}$$

In Eq. (P.18), ε_0 and μ_0 are the relative permittivity and permeability of free space, respectively. The former is a measure of the resistance of a medium (in this case, the 'vacuum') to the formation of an electric field—a certain fixed electric charge will generate a greater electric flux in a medium with low permittivity. The latter is a measure of the ability of a medium to support a magnetic field—applying a certain fixed magnetic field strength will result in greater magnetisation in a medium with high permeability.

Maxwell had made no assumptions about how these fields are supposed to move through space. But his equations not only demonstrate rather nicely the symmetry of the interdependent electric and magnetic fields, they also rather obviously describe wave motion. For a wave travelling in one dimension with velocity v, a generalized wave equation can be written as

$$\frac{\partial^2}{\partial x^2} \Psi(x, t) = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \Psi(x, t), \tag{P.19}$$

where $\Psi(x, t)$ is a generalized 'wavefunction'. From (P.18) and (P.19) we can deduce that $v = 1/\sqrt{\varepsilon_0 \mu_0}$. The velocity of Maxwell's 'electromagnetic waves' could now be determined from the experimental values of the relative permittivity and permeability of free space, which had been reported by German physicists Wilhem Weber and Rudolf Kohlrausch in 1856. Maxwell found that:[12]

> This velocity is so nearly that of light, that it seems we have strong reason to conclude that light itself (including radiant heat, and other radiations if any) is an electromagnetic disturbance in the form of waves propagated through the electromagnetic field according to electromagnetic laws.

But an electromagnetic disturbance in what? If we throw a stone into a lake, and watch as the disturbance ripples across the surface of the water, we conclude that the waves travel in a 'medium'—the water in this case. There could be no escaping the conclusion: electromagnetic waves had to be waves in some kind of medium. Maxwell himself didn't doubt that electromagnetic waves must move through the ether, a purely hypothetical, tenuous form of matter thought to fill all of space.

And here's another price to be paid. All the evidence from experimental and observational physics suggested that if the ether really exists, then it couldn't be participating in the motions of observable objects. The ether must be stationary. If the ether is stationary, then it is also by definition absolute: it fills precisely the kind of container demanded by an absolute space. A stationary ether would define the ultimate inertial frame of reference.

Newton required an absolute space that sits passively in the background and which, by definition, we can never experience. Now we have an absolute space that is supposed to be filled with ether. That's a very different prospect.

If the Earth spins in a stationary ether, then we might expect there to be an ether wind at the surface (actually, an ether drag, but the consequences are the same). The ether is supposed to be very tenuous, so we wouldn't expect to feel this wind like we feel the wind in the air. But, just as a sound wave carried in a high wind reaches us faster than a sound wave travelling in still air, we might expect that light travelling in the direction of the ether wind should reach us faster than light travelling against this direction. A stationary ether suggests that the speed of light should be different when we look in different directions.

Any differences were expected to be very small, but nevertheless still measureable with late-nineteenth-century optical technology. In 1887, American physicists Albert Michelson and Edward Morley performed experiments to look for such differences using a device called an interferometer, in which a beam of light is split and sent off along two different paths. The beams along both paths set off in phase, and they are then brought back together and recombined. Now, if the total path taken by one beam is slightly longer than the total path taken by the other, then when the beams are recombined, peak may no longer coincide with peak and the result is destructive interference. Alternatively, if the total paths are equal but the speed of light is different along different paths, then the result will again be interference.

But they could detect no differences. Within the accuracy of the measurements, the speed of light was found to be constant, irrespective of direction, suggesting that there is no such thing as a stationary ether. This is one of the most important 'negative' results in the entire history of experimental science.

Newton's laws of motion demand an absolute space and time that we can't experience or gain any empirical evidence for. Maxwell's electromagnetic waves demand a stationary ether to move in, but we can't gain any evidence for this either.

Atoms and the Second Law

The second law in question here is that of thermodynamics, the science born from the study of engines, and particularly the relationship between heat and work. French physicist and engineer Sadi Carnot is credited with establishing the basis for thermodynamics with his 1824 publication *Reflections on the Motive Power of Fire*, although some ten years passed before the merits of Carnot's work were realized by his fellow countryman Émile Clapeyron, who helped rid Carnot's theory of the concept of heat as a fluid, called caloric. Nine years later English physicist James Joule identified the mechanical equivalent of heat—motion and heat are equivalent and interchangeable—and helped to establish the law of conservation of energy. When Kelvin coined the term 'thermodynamics' in 1854, the conservation of energy was summarized as its first law.

Carnot had imagined that useful work can be derived as heat 'falls' from a higher temperature to a lower temperature, just as falling water will turn a paddle wheel. But Carnot imagined that heat would be conserved, meaning that all the usable heat is transferred into work without loss, allowing the possibility of perpetual motion and obviously in conflict with the conservation of energy. In 1850, German physicist Rudolf Clausius resolved this problem by declaring as a principle that heat cannot spontaneously flow from a cold object to a hot object, with the rest of the universe remaining unchanged.* For a system undergoing a closed cyclic process in which heat is transformed into work which is then transformed back into heat, Clausius expressed this principle mathematically as an inequality:

$$\oint \frac{\delta Q}{T} \leq 0. \tag{P.20}$$

In this equation the increments δQ represent the net amount of heat added to a system from an external reservoir at temperature T. For processes that are cyclical *and reversible*, meaning that infinitesimal changes that maintain thermodynamic equilibrium can in theory restore the initial state, the equality holds. But for processes that are irreversible the inequality holds. The logic here is fairly simple. In an irreversible process the (positive) heat input divided by the higher temperature *will always be smaller* than the (negative) heat output divided by the lower temperature. Summing (or integrating) over the cycle means $\delta Q/T < 0$.

Clausius was able to show that the ratio $\delta Q/T$ is a quantity which depends only on the physical state of the system, and not on the details of the path taken to produce it. Hence it is a *property* of the system, also called a function of state (or state function). In 1865 he went a little further, and identified this property as the *entropy* (symbol S) of the system, which he now defined for *reversible* open paths connecting some initial state i with a final state f, as

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* Kelvin formulated a similar principle at around the same time.

$$\Delta S_{rev} = S_f - S_i = \int_i^f dS_{rev} = \int_i^f \left(\frac{\delta Q}{T} \right)_{rev}. \tag{P.21}$$

The property of entropy accounts for the dissipative loss of heat (or energy) from the system, but to get a real sense for what this means we need to look at how Eqs. (P.20) and (P.21) can be combined. Equation (P.20) applies to a closed cycle which may involve paths that are reversible and/or irreversible, whereas (P.21) applies only to open paths that are reversible. So, imagine a closed cycle in which the path from initial to final state is irreversible, but the return path from final to initial state is reversible. From (P.20) we have

$$\oint \frac{\delta Q}{T} = \int_i^f \frac{\delta Q}{T} + \int_f^i \left(\frac{\delta Q}{T} \right)_{rev} \leq 0. \tag{P.22}$$

But the return path is reversible, and so from (P.21) we know that

$$\int_f^i \left(\frac{\delta Q}{T} \right)_{rev} = S_i - S_f. \tag{P.23}$$

Hence,

$$\int_i^f \frac{\delta Q}{T} + S_i - S_f \leq 0, \quad \text{or} \quad \Delta S_{irr} = S_f - S_i \geq \int_i^f \frac{\delta Q}{T}. \tag{P.24}$$

We see that the change in entropy from initial to final state in an irreversible process is *always greater* than the corresponding change for a completely reversible process, which is a direct consequence of applying Clausius' inequality. Heat transfer to a system increases its entropy, and heat transfer from a system will decrease its entropy, but factors that result in irreversibility (such as friction and other loss mechanisms) *will always increase the entropy*. We can see this more clearly by generalizing (P.24) for any irreversible process in an *isolated* system (one which doesn't exchange energy with the external environment). In such a situation $\delta Q = 0$ and

$$\Delta S_{irr} \geq 0, \tag{P.25}$$

which is a statement of the second law of thermodynamics.

This version of the second law was deduced by German physicist Max Planck in his 1879 doctoral thesis. He regarded it as a much more general statement, and so more fundamental and profound. For an isolated system energy will be conserved (first law) but entropy will inexorably increase to a maximum (second law) as the system achieves thermal equilibrium. Irreversibility and the increase in entropy are intimately linked, defining an 'arrow of time' such that any reverse process, spontaneously *decreasing*

entropy, implies running *backwards* in time, 'so that a return of the world to a previously occupied state is impossible'.[13]

And therein lies another problem.

As the science of thermodynamics was being worked out in the nineteenth century, so too was an elaborate mechanical theory of atoms. Hard, impenetrable, indestructible atoms, no more sophisticated than those imagined by the atomist philosophers of ancient Greece, had been an accepted metaphysical pre-commitment of seventeenth-century mechanical philosophers such as Newton. This despite the fact that they were not really necessary and did not feature in the classical mechanics that these philosophers helped to establish. Newton's atomism was quite influential in the eighteenth century, but as atoms appeared to lie well beyond the scope of any available experimental or observational technology, they remained firmly speculative.[14]

In 1738, the Swiss physicist Daniel Bernoulli had argued that the properties of gases could be understood to derive from the rapid motions of the innumerable atoms or molecules that constitute the gas (hereafter referred to simply as 'atoms'). Gas pressure then results from the *impact* of these atoms on the surface of the vessel that contains them. Gas temperature is the result of the *motions* of the atoms. This *kinetic theory of gases* bounced around for a few decades before being refined by Clausius in 1857. Two years later Maxwell developed a mathematical formula for the distribution of the velocities of the atoms in a gas. As it is obviously impossible to keep track of the motions of large numbers of individual atoms, Maxwell was obliged to resort to probabilities and so derived a probability distribution. This was generalized in 1871 by Austrian physicist Ludwig Boltzmann, and is now known as the Maxwell–Boltzmann distribution.

Boltzmann built further on Maxwell's ideas, applying probabilities to the distribution of *energy* instead of velocity, as he worked to derive all the most important thermodynamic quantities based on the underlying motions of the system's constituent atoms. In 1877 he derived the expression for the entropy of an ideal gas which is carved on his gravestone,

$$S = k_B \ln(W), \tag{P.26}$$

where k_B is Boltzmann's constant and W is the number of microstates (the number of individual configurations of atomic positions and velocities or momenta that are possible). If it is assumed that all these microstates are equally probable, then the probability for each microstate is simply $1/W$. Bulk quantities such as pressure, temperature, and entropy summarize the macrostate of the system.

The second law can now be interpreted as the natural evolution of an isolated system towards the largest number of available microstates. If we pump a gas into one corner of an otherwise empty container, we anticipate that this system will evolve dynamically: the gas will expand and become diluted so that it fills all of the available space. The number of microstates (atomic positions and momenta) that are available in the final equilibrium situation is much greater than in the initial situation. Entropy increases.

We can now see how Hamiltonian mechanics is perfectly suited to the interpretation of thermodynamics in terms of complex systems involving the motions of large numbers of atoms. In his *Lectures on Gas Theory*, published in 1896, Boltzmann himself defined

'phase' to mean the collective state of a gas derived from the positions and momenta of all its constituent atoms, though he held back from calling it phase space.[15]

But towards the end of the nineteenth century the existence of atoms was still largely a matter for metaphysical speculation and many physicists were inclined to be rather stubborn about them. It's perhaps difficult for readers who have lived with the fallout from the 'atomic age' to understand why perfectly competent scientists should have been so reluctant to embrace atomic ideas, but we must remember that by 1900 there was very little evidence for their existence. Some physicists, such as the arch-empiricist Mach, rejected them completely. To make matters considerably worse, the statistical mechanical interpretation of thermodynamics produced conclusions which some physicists found extremely discomforting.

Statistics have a dark side. They deal with *probabilities*, not certainties. What thermodynamics argues to be unquestionably irreversible and a matter of irresistible natural law, statistics argues that this is only the most probable of many different possible alternatives. The conflict was most stark in the interpretation of the second law and in 1895, with Planck's approval, his research assistant Ernst Zermelo took the argument directly to the atomists in the pages of the German scientific journal *Annalen der Physik*.

If we were to release two gases of different temperature in a closed container, the second law predicts that the gases will mix and the temperature will become uniform, with the entropy of the mixture increasing to a maximum. However, according to the atomists, the behaviour of the gases is a consequence of the underlying mechanical motions of the atoms of each gas, and the equilibrium state of the mixture is simply the most probable of many possible states. Furthermore, such dynamical systems could be expected to exhibit Poincaré recurrence, implying that, if we wait long enough, the system will eventually return to its initial far-from-equilibrium state, with the gases once more separated at different temperatures. Such a possibility runs directly counter to the second law, which insists that in an isolated system undergoing spontaneous change, entropy can never decrease, Eq. (P.25).

Boltzmann had no real alternative but to accept what statistical mechanics implied. Entropy does not always increase, he argued, in contradiction to the most common interpretation of the second law. It just almost always increases. Statistically speaking, there are many, many more states of higher entropy than there are of lower entropy, with the result that the system spends much more time in higher entropy states. In effect, Boltzmann was saying that if we do indeed wait long enough, we might eventually catch a system undergoing a spontaneous reduction in entropy. This is as miraculous an event as a smashed cocktail glass spontaneously reassembling itself, to the astonishment of party guests.

To Planck, this stretched the interpretation of his cherished second law to breaking point. It may have been that Planck was not averse to the atomic theory per se—he was certainly well aware of the theory's successes. But he judged that it was unlikely to offer a productive approach to a deeper understanding of thermodynamics. In a letter to Wilhelm Ostwald in 1893 he declared that the atomic theory was nothing less than a 'dangerous enemy of progress'.[16] Matter is continuous, not atomic, he insisted. He had no doubt that atomic ideas would eventually have to be abandoned, despite their

success, 'in favour of the assumption of continuous matter'.[17] In his historical analysis, American philosopher Thomas Kuhn argues that Planck's 'continuous medium' would subsequently become the ether.[18]

In seeking to find a way to refute Boltzmann's statistical arguments, Planck chose as a battleground the physics of 'black body' radiation. And this is where our story really begins.

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NOTES

1. See, for example, Walter Isaacson, *Einstein: His Life and Universe*, Simon & Schuster, London, 2007, p. 90.
2. Although this statement is widely attributed to Kelvin, Isaacson could find no evidence to suggest that Kelvin had actually said it. See Isaacson, *Einstein*, p. 575.
3. A. A. Michelson, *Light Waves and Their Uses*, University of Chicago Press, Chicago, 1903, p. 24.
4. In April 1900 Kelvin delivered a lecture to the Royal Institution in London in which he declared that there were several 'clouds' over the dynamical theory of heat and light. See Helge Kragh, *Quantum Generations: A History of Physics in the Twentieth Century*, Princeton University Press, Princeton NJ, 1999, p. 6.
5. Isaac Newton, letter to Robert Hooke, 15 February 1676. See: https://digitallibrary.hsp.org/index.php/Detail/objects/9792
6. Gottfried Wilhelm Leibniz, from his correspondence with Samuel Clarke (1715–16), *Collected Writings*, edited by G. H. R. Parkinson, J. M. Dent & Sons, London, 1973, p. 226.
7. Isaac Newton, *Mathematical Principles of Natural Philosophy*, first American edition translated by Andrew Motte, published by Daniel Adee, New York, 1845, p. 73.
8. Ernst Mach, *The Science of Mechanics: A Critical and Historical Account of Its Development*, 4th edition, translated by Thomas J. McCormack, Open Court Publishing, Chicago, 1919, p. 194 (first published 1893). See also Max Jammer, *Concepts of Mass in Contemporary Physics and Philosophy*, Princeton University Press, Princeton, NJ, 2000, p. 11; and O. Bellkind, *Physical Systems*, Boston Studies in the Philosophy of Science, **264** (2012), 119–44.
9. Gottfried Wilhelm Leibniz, *New Essays on the Human Understanding*, reproduced in *Collected Writings*, ed. Parkinson, p. 167.
10. Newton, *Mathematical Principles*, p. 506.
11. This quote is taken from Henry Brougham, *The Edinburgh Review, or Critical Journal*, **1**, January 1803, pp. 450–6. This was an anonymous review, but Young correctly identified the author as Brougham, then a barrister and later Lord Chancellor of England. For more details on the controversy, see Christine Simon, 'Thomas Young's Bakerian Lecture', *The Fortnightly Review*, 2014: http://fortnightlyreview.co.uk/2014/09/thomas-young/#fnref-13923-13
12. J. Clerk Maxwell, 'A Dynamical Theory of the Electromagnetic Field', *Philosophical Transactions of the Royal Society of London*, **155** (1865), 466.
13. This statement appears in the very first introductory paragraph of Planck's thesis, *Über den zweiten Hauptsatz der mechanischen Wärmetheorie* (On the Second Law of Thermodynamics), 1879. Quoted in Thomas S. Kuhn, *Black-body Theory and the Quantum Discontinuity 1894–1912*, University of Chicago Press, Chicago, 1978, p. 16.

15. David D. Nolte, 'The Tangled Tale of Phase Space', *Physics Today*, April 2010, 33–8.
16. Max Planck, letter to Wilhelm Ostwald, 1 July 1893. Quoted in J. L. Heilbron, *The Dilemmas of an Upright Man: Max Planck and the Fortunes of German Science*, Harvard University Press, Cambridge, MA, 1996, p. 15.
17. Max Planck, *Physikalische Abhandlungen und Vorträge*, Vol. 1, Vieweg, Braunschweig, 1958, p. 163. Quoted in Heilbron, *Dilemmas*, p. 14.
18. Kuhn, *Black-body Theory*, p. 23.

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Planck's Derivation of $E = h\nu$

The Quantization of Energy

Planck was born in Kiel in April 1858, descended from a line of pastors and professors of theology and jurisprudence. At school Planck was diligent and personable but not especially gifted. Physics was a subject for which Planck himself felt he had no particular talent, and he had once been counselled against a career in theoretical physics. His professor at the University of Munich had advised him that, with the discovery of the principles of thermodynamics, physics as a subject had been largely completed. There was, quite simply, nothing more to be discovered.[1] This was fine with Planck, who was quite content with the rather less heroic task of deepening the foundations of science. He had no real interest in making new discoveries.

He preferred the stability and predictability of a science which reflected the character of the bourgeois German society of which he was a part. He had risen through the academic ranks and established a solid international reputation as a master of classical thermodynamics, and especially the second law. Now in his early forties, he worked at a slow, steady, and conservative pace. By his own subsequent admission, he was 'peacefully inclined', and rejected 'all doubtful adventures'.[2]

Planck is thus a good candidate for the history of science's most unlikely revolutionary.

Black Body Radiation

As we saw in the Prologue, Planck was unwilling to accept Boltzmann's statistical interpretation of the second law. He therefore needed to find a way to show how irreversible processes could result from matter that forms a continuum. Such a continuum would exhibit some kind of collective, ordered, or correlated motion, in contrast to the disordered motions characteristic of the atoms of Maxwell and Boltzmann. Irreversibility would then be associated with changes in this collective motion; changes that are not described by resorting to arguments based on probabilities, which opens the door to unacceptable, entropy-reducing processes, no matter how improbable they may be. Although Planck had chosen to reject atoms, he held firm to the theory of mechanics, and in this way he hoped eventually to reconcile mechanics with thermodynamics.

That Planck should turn his attention from the thermodynamics of gases to the physics of black body radiation as a battleground might seem puzzling at first. But Planck saw no contradiction. To understand why, we first need to know a little more about it.

Heat any object to a high temperature and it will glow, emitting light of different colours. We say that the object is 'red hot' or 'white hot'. Increasing the temperature of the object increases the intensity of the light and shifts it to a higher range of frequencies (shorter wavelengths). As it gets hotter, an object glows first red, then orange-yellow, then bright yellow, then brilliant white.

Theoreticians had sought to model the physics based on the notion of a black body, a completely non-reflecting object that is presumed to absorb and emit light radiation perfectly, without favouring any particular range of radiation frequencies or wavelengths (or colours). The density or intensity of the radiation that a black body emits, measured over a range of frequencies, is then directly related to the amount of energy it contains.

The properties of black body radiation could be studied in the laboratory using specialized cavities, vessels made of porcelain and platinum with almost perfectly absorbing walls. Such cavities could be heated, and the radiation released and trapped inside could be observed with the aid of a small pinhole, a bit like peeking into the glowing interior of an industrial furnace. Such studies provided more than just an interesting test of theoretical principles. Cavity radiation was also useful to the German Bureau of Standards as a reference for rating electric lamps.

Planck imagined that the source of the (continuous) electromagnetic radiation released into the cavity is a continuum of ideal mechanical vibrators, or 'resonators'. These resonators were entirely imaginary, their sole purpose being to absorb and emit radiation and so bring the system—cavity and radiation—to a dynamic equilibrium. The radiation would have an entropy—just like a gas—and equilibrium would be characterized by maximum entropy.

Consequently, Planck wasn't specific on where these resonators might be physically located, but if it helps, we can suppose they reside in the cavity material. We probably wouldn't hesitate today to identify these with the electrons in the atoms of the material, but remember that the electron was only discovered in 1895 and in 1900 Planck was strenuously opposed to the idea of atoms. For now, let's not worry overmuch about what these resonators might actually represent.

Planck subsequently acknowledged that the use of the term 'resonators' was inappropriate (a resonator oscillates only at specific—resonant—frequencies). These imaginary objects are actually so-called 'linear Hertzian oscillators', which we can think of as massless springs with electric charge at each end. Planck's task was to show how irreversible processes (and the second law) could arise from the collective motions of the oscillators and the dynamic exchange of energy between the oscillators and the trapped radiation. No atoms to be seen, anywhere.

This must have seemed like a perfectly safe choice.

In the winter of 1859–60, the German physicist Gustav Kirchhoff had demonstrated that the ratio of emitted to absorbed radiation energy depends only on the frequency of the radiation and the temperature inside the cavity. This means that the density of radiation inside the cavity at equilibrium is a function only of frequency, ν, and

temperature, T, designated $\rho(v, T)$. The density does not depend in any way on the shape of the cavity, the shape of its walls, or the nature of the material from which the cavity is made. This implied that something quite fundamental concerning the physics of the radiation itself was being observed, and Kirchhoff challenged the scientific community to discover the origin of this behaviour.

Planck's Radiation Law

Much progress had been made. Studies of infrared (heat) radiation had in 1896 led German physicist Wilhelm Wien to devise Wien's law, which can be summarized (in modern notation) as follows:

$$\rho(v, T) = \frac{8\pi h v^3}{c^3} e^{-hv/k_B T},\tag{1.1}$$

where c is the speed of light and h and k_B would later become known as Planck's constant and Boltzmann's constant, respectively. The real significance of these physical constants was not immediately apparent.

Wien's law seemed to be quite acceptable, and was supported by further experiments carried out by German physicist Friedrich Paschen at the Technical Academy in Hanover in 1897. But new experimental results reported in 1900 by Otto Lummer and Ernst Pringsheim at the Reich Physical-Technical Institute in Berlin showed that Wien's law failed at lower frequencies. Wien's law was clearly not the answer.

In June 1900, English physicist Lord Rayleigh (William Strutt) published details of a new theoretical model based on the 'modes of ethereal vibration' in the cavity. Each mode was supposed to possess a specific frequency, and could take up and give out energy continuously. Rayleigh assumed a classical distribution of energy over these modes. At equilibrium, each mode of vibration should then possess an energy directly proportional to the cavity temperature.

It's instructive to interrupt this historical narrative and fast-forward a few years to May 1905. Rayleigh obtained an expression for the constant of proportionality, but made an error in his calculation which was put right by James Jeans the following July. The result is now known as the Rayleigh–Jeans law:

$$\rho(v, T) = \frac{8\pi v^2}{c^3} k_B T.\tag{1.2}$$

Rayleigh's reasoning and use of thermodynamic principles was both logical and convincing, but the result was disastrous. The Rayleigh–Jeans law implies that $\rho(v, T)$ increases with the square of the radiation frequency without limit, and so the total emitted energy quickly mushrooms to infinity at high frequencies. In 1911 the Austrian physicist Paul Ehrenfest called this problem the 'Rayleigh–Jeans catastrophe in the ultraviolet', now commonly known as the *ultraviolet catastrophe*. Rayleigh's approach might have been perfectly logical, but the result was totally illogical.

But both Wien's law and the Rayleigh–Jeans law were glimpses of the complete picture, approximations of $\rho(v, T)$ applicable only at the extremes of high and low radiation frequency.

Planck had succeeded Kirchhoff at the University of Berlin in 1889, rising to full professor in 1892. He was unaware of Rayleigh's work when, on 7 October 1900, German physicist Heinrich Rubens visited him at his villa in the Berlin suburb of the Grünewald. Rubens told him about some new experimental results he had recently obtained with his associate Ferdinand Kurlbaum.

Rubens and Kurlbaum had studied cavity radiation at even lower frequencies, and the behaviour they had observed set Planck thinking. After Rubens had left, Planck continued to work alone in his study. After some reflection, he found that he could now replace Wien's law with one of his own, 'a result of inspired guesswork, scientific tact, sober compromise, in short, of tinkering':[3]

$$\rho(v, T) = \frac{8\pi h v^3}{c^3} \frac{e^{-hv/k_B T}}{1 - e^{-hv/k_B T}}. \tag{1.3}$$

This result is shown graphically in Fig. 1.1. We can now see what happens. For very *high* v (or short wavelengths), the term $e^{-hv/k_B T}$ becomes very small compared with 1 and Planck's radiation law reduces to Wien's law. If we multiply the exponential term in Planck's law top and bottom by $e^{hv/k_B T}$, we can re-write this term as $1/(e^{hv/k_B T} - 1)$.
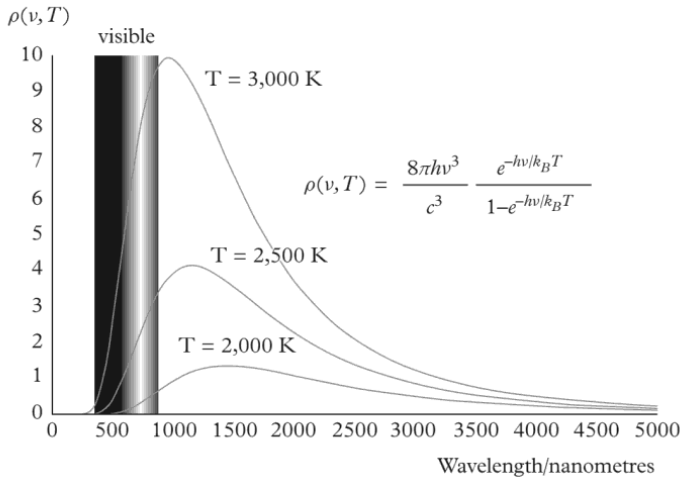

Figure 1.1 *Planck's radiation law predicts the variation of radiation density with frequency or wavelength at different cavity temperatures. As the temperature increases, the peak wavelength shifts to shorter and shorter values.*

For very *low* v (long wavelengths), $e^{hv/k_B T}$ can be approximated as $1 + hv/k_B T$, and Planck's law reduces to the Rayleigh–Jeans law.

Planck sent Rubens a postcard summarizing details of his new radiation law, and he presented a crude derivation at a meeting of the German Physical Society on 19 October. He declared: 'I therefore feel justified in directing attention to this new formula, which, from the standpoint of electromagnetic radiation theory, I take to be the simplest excepting Wien's.'[4] The next day, Rubens advised Planck that he had compared the experimental results with the new law and found 'completely satisfactory agreement in all cases'.[5]

But, although Planck's new law was satisfactory, it was in truth no more than a mathematical 'fit' to the data. Planck's challenge now was to find a deeper theoretical interpretation for it, and of course to make use of this interpretation to pursue his principal objective, which was to reconcile mechanics and thermodynamics and reassert the irreversible nature of the second law.

The Oscillator Energy

To follow Planck's logic we need to understand the nature of the relationships between $\rho(v, T)$ and thermodynamic quantities such as the internal energy U and entropy S of the cavity radiation. These latter quantities are, of course, inter-related.

According to the first law of thermodynamics the microscopic change in the internal energy of the radiation dU is equal to the amount of heat absorbed (δQ) less any work done. But the cavity radiation does no work (it's not used to drive a piston, for example), so $dU = \delta Q$; the change in internal energy logically derives only from the heat absorbed.

We know from Eq. (P.21) that $dS = \delta Q/T$, so in this situation $dU = TdS$, which is a version of the so-called fundamental thermodynamic relation. We can therefore get to the entropy from

$$dS = \frac{1}{T}dU \tag{1.4}$$

and integrating.

We can suppose that the frequency of vibration of the imaginary oscillators increases with increasing temperature and they exchange energy with the radiation *at the same frequency* with which they are vibrating. If we assume that *all* the energy of the oscillators is released into the cavity radiation, then at thermodynamic equilibrium we can further suppose that the internal energy (and entropy) of the oscillators is identical to that of the radiation. Consequently, Planck focused on the relationship between $\rho(v, T)$ and the average internal energy of the oscillators themselves (which we will refer to here as $U(v, T)$.

Between 1897 and 1899, Planck published a series of five papers titled 'On Irreversible Radiation Processes', in which he analysed a model system consisting of electromagnetic

was indispensable to me, is that according to it the energy of the resonant oscillator depends only on radiation intensity and frequency ν but not on any of its other properties.'[6]

There are a number of different ways to derive Eq. (1.5), but perhaps the simplest involves the analysis of the radiation in terms of cavity modes, as explained in Appendix 1. Interestingly, if we assume that the oscillators are all identical and follow a simple harmonic motion, then we know that the total average thermal energy of each oscillator consists of contributions of $\frac{1}{2}k_B T$ from translational motion (kinetic energy) and $\frac{1}{2}k_B T$ from its potential energy. This is the *equipartition theorem*, developed in the 1840s, which relates the temperature of a system to its average energies. Under this assumption, we see that $U(\nu, T)$ is independent of ν and equal to $k_B T$, which on substitution in Eq. (1.5) gives the Rayleigh–Jeans law.

So, in May 1899 Planck had access to a really rather simple and straightforward route to the Rayleigh–Jeans law, more than a year before Rayleigh himself published his (erroneous) version of it. However, it seems that, at this time, Planck was simply unaware of the equipartition theorem.

In any case, we know that the Rayleigh–Jeans law is physically unrealistic except as a low-frequency limit. Comparing Eq. (1.5) with Planck's radiation law (1.3) shows that $U(\nu, T)$ is much more complicated than the equipartition theorem would suggest, and is indeed dependent on both ν and T:

$$U(\nu, T) = \frac{h\nu e^{-h\nu/k_B T}}{1 - e^{-h\nu/k_B T}} = \frac{h\nu}{e^{h\nu/k_B T} - 1}. \tag{1.6}$$

Planck's task was now to make use of Eq. (1.6) to derive an expression for the average entropy of the oscillators, one that would be entirely consistent with his radiation law. This was to lead to 'some weeks of the most strenuous work of my life'.[7] Planck tried several different approaches, but he found that he was compelled to return to the statistical methods of his arch-rival Boltzmann. The mathematics led him in a direction he really did not want to go. He eventually succumbed, in a final act of desperation. As he later admitted: 'A theoretical interpretation therefore *had* to be found at any cost, no matter how high'.[8]

Although the approach Planck took was subtly different from that of Boltzmann, as we will see, he found that black body radiation is absorbed and emitted *as though* it is composed of discrete 'atoms', which Planck called *quanta*. Moreover, he found that each quantum of radiation has a fixed energy given by $E = h\nu$. Though much less familiar, this is an expression that is every bit as profound as Einstein's $E = mc^2$.

So, what did Planck do?

The Ingredients

1. Integration by substitution.
2. The standard integral of $\ln(x)$.

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So, what did Planck do?

The Ingredients

1. Integration by substitution.
2. The standard integral of $\ln(x)$.
3. Boltzmann's equation for the entropy: $S = k_B \ln(W)$.
4. Combinatorics: partition theory.
5. Stirling's formula for the factorials of large numbers: $N! = (N/e)^N$.

The Recipe

It is perhaps a little unfortunate that this first recipe—the recipe that launched the quantum revolution—is somewhat convoluted and rather more difficult to follow than some of the other iconic equations of quantum mechanics. But this really shouldn't come as too much of a surprise. Thermodynamics is not the most obvious place to look for evidence of the quantum nature of radiation, and Planck had to torture the theory in a way that would eventually allow this conclusion to emerge from an entirely classical structure. It was always going to be a difficult birth.

We begin in Step (1) by manipulating the expression for the average internal energy of an oscillator, Eq. (1.6), such that it is in a form that can be more easily integrated. On integration we will have an expression for the entropy of an oscillator which is consistent with Planck's radiation law and which we can then generalize for a large collection of N oscillators. We can think of this as a derivation of the entropy based on thermodynamics which we know to be consistent with experimental data (as summarized by Planck's law).

As Planck soon realized, the result looks to all the world like a version of Boltzmann's equation for the entropy, based on the logarithm of the number of microstates, or the number of different possible configurations, W, as given in Eq. (P.26).

But the possible configurations of what, exactly? After all, there are no atoms or atomic motions in this system. So, in Step (2) we take another route, calculating the entropy using Boltzmann's methods but with a not-so-subtle difference. Boltzmann estimated the number of possible microstates W as the number of different ways that the available energy can be distributed over a large number of *distinguishable* atoms. But this couldn't give Planck the mathematical form demanded by the expression for the entropy which he had deduced in Step (1). So he did something different. He instead estimated W as the number of ways in which a series of *indistinguishable* energy elements can be distributed over a large number of oscillators.

We can think of this as a derivation of the entropy based on statistics. In his biography of Einstein, the American physicist Abraham Pais wrote: 'From the point of view of

physics in 1900 the logic of Planck's electromagnetic and thermodynamics steps was impeccable, but his statistical step was wild."[9]

Our final Step (3) is simply to compare the two derivations of the oscillator entropy and draw conclusions.

Step (1): Derive the Oscillator Entropy from Thermodynamics

Our starting point is the expression for the average internal energy of an oscillator which we know to be consistent with Planck's radiation law, Eq. (1.6). As this next bit is going to get complicated, let's simplify the notation, replacing $U(v, T)$ with U, but remembering that U is a function of both frequency and temperature. We can rearrange the expression we got for U in Eq. (1.6) as follows:

$$U e^{hv/k_B T} - U = hv \quad \text{or} \quad U e^{hv/k_B T} = hv + U. \tag{1.7}$$

Taking natural logarithms of both sides of this last expression gives

$$\ln(U) + \frac{hv}{k_B T} = \ln(hv + U), \tag{1.8}$$

which we can rearrange to give an expression for $1/T$:

$$\frac{1}{T} = \frac{k_B}{hv} \left[\ln(hv + U) - \ln(U) \right]. \tag{1.9}$$

We can tidy this up a bit by recognizing that

$$\ln(hv + U) = \ln\left(1 + \frac{U}{hv} \right) + \ln(hv) \tag{1.10}$$

and

$$\ln(U) = \ln\left(\frac{U}{hv} \right) + \ln(hv). \tag{1.11}$$

When we put these into the expression for $1/T$ the terms in $\ln(hv)$ cancel and we get

$$\frac{1}{T} = \frac{k_B}{hv} \left[\ln\left(1 + \frac{U}{hv} \right) - \ln\left(\frac{U}{hv} \right) \right]. \tag{1.12}$$

We can now substitute this expression for $1/T$ directly into the expression for dS, Eq. (1.4):

$$dS = \frac{k_B}{hv}\left[\ln\left(1 + \frac{U}{hv}\right) - \ln\left(\frac{U}{hv}\right)\right]dU. \tag{1.13}$$

To obtain an expression for the average oscillator entropy we need to integrate

$$S = \frac{k_B}{hv}\int\left[\ln\left(1 + \frac{U}{hv}\right) - \ln\left(\frac{U}{hv}\right)\right]dU. \tag{1.14}$$

This looks pretty complicated, but we can simplify it by making a couple of substitutions:

$$x = 1 + \frac{U}{hv} \quad \text{for which} \quad \frac{dx}{dU} = \frac{1}{hv} \quad \text{and} \quad dU = hv\,dx \tag{1.15}$$

and

$$y = \frac{U}{hv} \quad \text{for which} \quad \frac{dy}{dU} = \frac{1}{hv} \quad \text{and} \quad dU = hv\,dy. \tag{1.16}$$

Making these substitutions transforms the expression for S into

$$S = k_B\left[\int(\ln(x)\,dx - \ln(y)\,dy)\right]. \tag{1.17}$$

We can now use the standard integral $\int\ln(x)\,dx = x\ln(x) - x$ to give

$$S = k_B\left[\left(1 + \frac{U}{hv}\right)\ln\left(1 + \frac{U}{hv}\right) - \left(1 + \frac{U}{hv}\right) - \frac{U}{hv}\ln\left(\frac{U}{hv}\right) + \frac{U}{hv}\right] + C, \tag{1.18}$$

where C is a constant of integration.

The free terms U/hv cancel, and the extra term $-k_B$ can be absorbed into the constant, leaving us with

$$S = k_B\left[\left(1 + \frac{U}{hv}\right)\ln\left(1 + \frac{U}{hv}\right) - \frac{U}{hv}\ln\left(\frac{U}{hv}\right)\right] + C'. \tag{1.19}$$

The final step involves one last bit of rearranging, to give

$$S = k_B\ln\left[\frac{\left(1 + \frac{U}{hv}\right)^{1+U/hv}}{\left(\frac{U}{hv}\right)^{U/hv}}\right] + C'. \tag{1.20}$$

The entropy of N oscillators is obviously N times the average entropy of one oscillator, and we quietly set aside the constant C', as measures of entropy are based on differences in which any constant contributions will subtract out:

$$S_N = Nk_B \ln \left[\frac{\left(1 + \frac{U}{h\nu}\right)^{1+U/h\nu}}{\left(\frac{U}{h\nu}\right)^{U/h\nu}} \right]. \tag{1.21}$$

This is almost certainly *not* where Planck had hoped to get to. The term in square brackets in Eq. (1.21) is, as we will soon see, strongly reminiscent of a combinatorial expression, implying that this is nothing less than a version of Boltzmann's equation for the entropy, $S = k_B \ln(W)$. The mathematics had taken Planck in a direction he really had not wanted to go.

Planck had been fighting a losing battle against Boltzmann's logic for at least three years. He now succumbed to the inevitable. As he later explained: 'I busied myself, from then on, that is, from the day of its establishment, with the task of elucidating a true physical character for the [new radiation law], and this problem led me automatically to a consideration of the connection between entropy and probability, that is, Boltzmann's trend of ideas.'[10]

Step (2): Derive the Oscillator Entropy from Statistics

Boltzmann reasoned that the most probable state of a gas at thermal equilibrium is the one with the highest number of different ways to distribute (or *partition*) the available energy over the atoms or molecules of the gas, representing the maximum entropy at that energy. In essence, the second law of thermodynamics ensures that energy is distributed 'fairly' over all the particles that can carry it. In other words, it doesn't accumulate in a subset of these, equivalent to a small quantity of the gas (let's say the air in one corner of the room where you're sitting) spontaneously becoming hotter than the rest. As we've discussed already in the Prologue, this isn't completely ruled out by Boltzmann's logic; it's just that such a situation is very highly improbable. By working out the maximum number of possible ways to partition the energy (which Boltzmann called the number of *complexions*), it is a relatively simple step to calculate the entropy.

Boltzmann's approach to such a calculation involves assuming that the total available (and continuously variable) energy in a system can be thought of as being organized into a series of 'buckets'. The lowest energy bucket is assigned an energy E, the next an energy $2E$, the next $3E$, and so on. The atoms of the gas are then distributed among the buckets and the number of different possible permutations of atoms in the buckets is calculated. In this analysis the use of buckets is simply a calculation tool, with no real physical significance intended. All that Boltzmann had done was parcel up the energy so that he could count the number of atoms *in the energy range* zero to E, the range E to $2E$, the range $2E$ to $3E$, and so on, and thus calculate the number of different possible permutations.

For example, consider a gas consisting of just three atoms, which we assume are distinguishable and which we label *a*, *b*, and *c*. Let's assume this gas has a total energy of $4E$. We can't put all three atoms in the lowest energy bucket, as this doesn't account

where N is the number of particles, n_i is the 'occupation number' (the number of atoms in the ith energy bucket), and P is the total number of buckets. In the simple example given above $N = 3$ and $N! = 6$. The number of particles in energy bucket 1 is 2 (so $n_1 = 2, 1/n_1! = 1/2! = 1/2$) and the number of particles in energy bucket 2 is 1 (so $n_2 = 1, 1/n_2! = 1/1! = 1$). W is then equal to $6 \times \frac{1}{2} \times 1 = 3$. Incidentally, if we assume each of these permutations is equally probable, then the probability for each permutation is simply $1/W = 1/3$.*

It obviously gets more interesting as the number of atoms and the amount of energy increases. In the case of $8E$ distributed over 5 atoms, we can see that there are two possibilities, also shown in Fig. 1.2. In one of these we put 2 atoms in energy bucket 1 and 3 in energy bucket 2, giving the number of permutations $W = 10$. However, putting 3 particles in bucket 1, 1 in bucket 2, and 1 in bucket 3 increases W to 20. Nature will favour the combination which maximizes the complexity at equilibrium (i.e. minimizes the product of the $n_i!$ in the denominator), and hence the entropy.
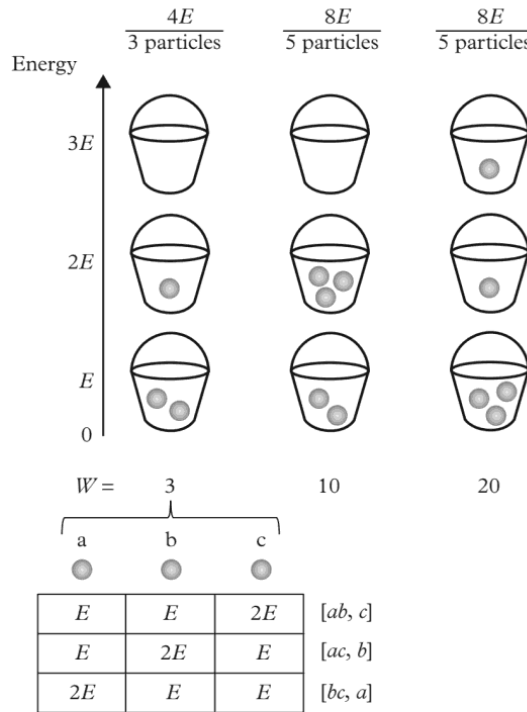

Figure 1.2 *In Boltzmann's approach the total available energy in a system is assumed to be continuously variable but organized into a series of 'buckets'. This makes it possible to count the number of atoms in the energy range zero to E, E to 2E, 2E to 3E, and so on. The entropy is then calculated from the maximum number of possible permutations, W. Note that in this method of counting, no molecule is assigned zero energy.*

* Note that if we relax the restriction to conserve energy, Eq. (1.22) implies many more possible permutations than we're considering here.