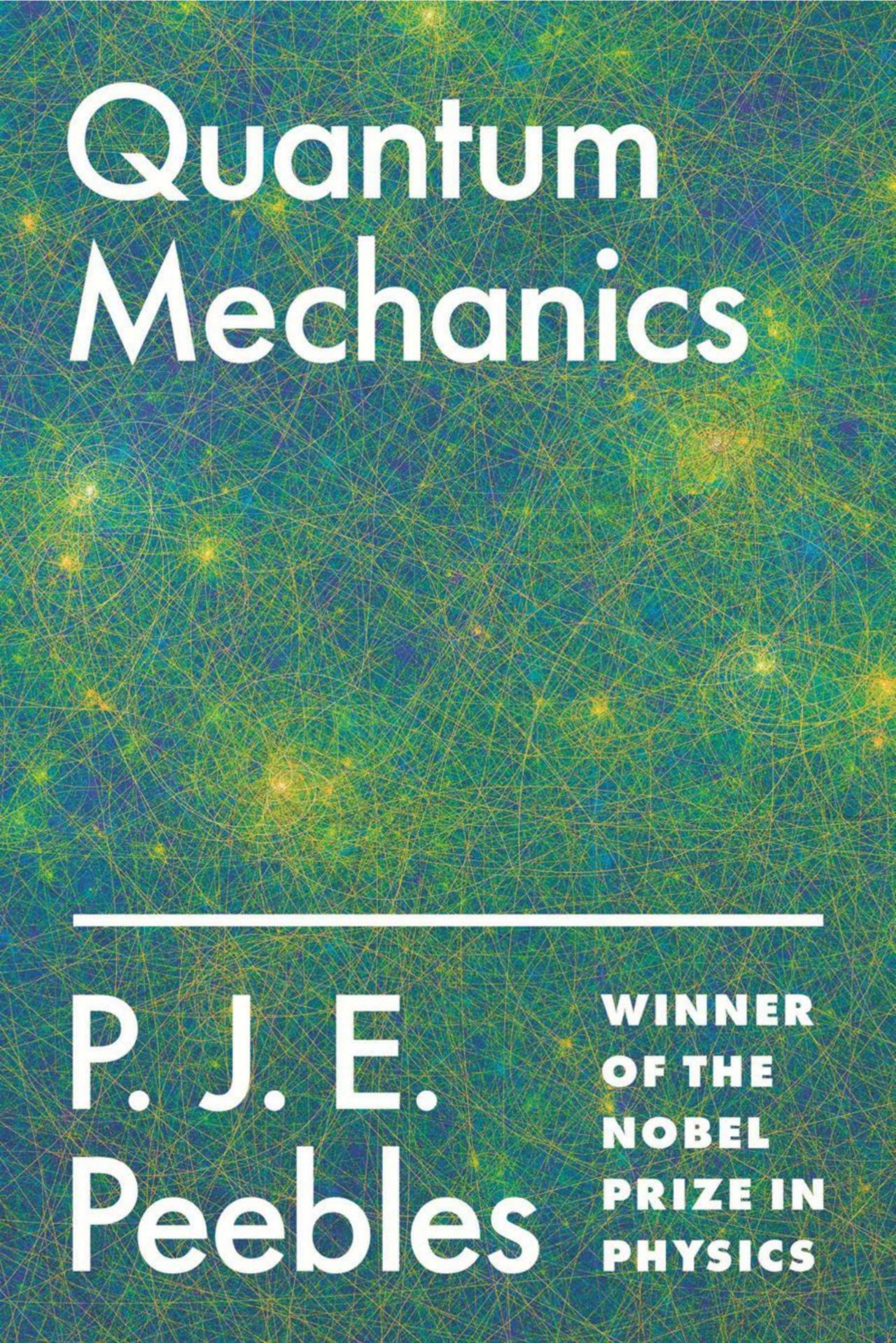

Quantum Mechanics

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WINNER OF THE NOBEL PRIZE IN PHYSICS

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Preface

To understand quantum mechanics one ought to see how this remarkable world picture was discovered, and one must work through the details of some nontrivial applications that show how the theory works. Most of us also require a good deal of practice working physically interesting problems. My approach in this book, that grew out of a heavy but I hope not impossibly hard one-year course, is to introduce the full details of the theory as needed, so one can see specific and interesting applications, and to make room for this by dropping things like the analysis of special functions that are not important for the chosen applications. My hope is that this book will find a niche between introductory surveys, that can give some idea of what is going on but may leave the reader with the feeling that there are mysterious corners to the theory, and the standard treatises, which contain more than most of us want to know about quantum mechanics.

My arrangement of material roughly follows standard precedents, but with some exceptions that should be explained. The first chapter presents the origins of quantum mechanics in the usual pseudohistorical style of physics. It is important to convince the reader that the theory was not derived from measurements, nor discovered by a single theoretical stroke, but instead grew by a complicated interplay of experimental hints, theoretical insights, and good luck, intermingled with many wrong turns. An adequate study of this development would take a whole course; the survey presented here is misleading because it ignores the wrong turns, and incorrect because it doesn't even present the main advances in the right order, but there is not time to do better. Instead, I attempt to give some flavor of what went on by presenting a set of examples of physics that are well worth knowing independent of their historical interest. Here, and throughout the book, sections marked by an asterisk contain material I do not always include in the course for lack of time. For example, I like the treatment of phonons in section 12c as an introduction to the eigenvalue problem, but usually conclude that it takes more time than I can afford.

I hope the introductory chapter shows how people could have hit on wave mechanics, if not how it really happened. Chapter 2 develops the wave mechanics formalism. The emphasis here is on symmetries and conservation laws: parity, linear and angular momentum, and the electromagnetic interaction. The only specific physical application is the completion of the study of an isolated hydrogen atom, with some discussion of the motion of a particle in a magnetic field. This is a little dry, but of course it is needed if one is to do grown-up quantum mechanics, and I think the symmetry methods are clarified by presenting the standard cases all in the same chapter.

The formal development could end here, but I find it more satisfying, and not a lot more time consuming, to redevelop the theory in the abstract Dirac bracket formalism. It is fairly easy, and I think fascinating, to see how wave mechanics follows from the position representation and the canonical commutation relations. The main new application in this chapter is the treatment of spin.

At this point, which is about midway in the course, one is ready to practice quantum mechanics by applying it to real physical problems, but I think it is good to pause and consider measurement theory. Since this undoubtedly is part of the physics, it is striking to see how little space is devoted to it in many of the standard books (with notable exceptions, including David Bohm's *Quantum Theory*, and some more recent books such as Hans Ohanian's *Principles of Quantum Mechanics*). One reason is easy to see: a physicist can spend a career working on quantum mechanics without thinking about measurement theory beyond the bare prescription that can be written down in a few paragraphs. Another likely reason is that the attempt to decide what the measurement prescription really is telling us about the deeper nature of physical reality is a slippery business that so far has led to no fully satisfying conclusion. But much the same is true of any open research problem, and a discussion of open questions in the measurement puzzle may be a useful antidote to our tendency in physics textbooks to gloss over complexities. There is considerably more material on measurement theory in chapter 4

Quantum Mechanics

CHAPTER 1

HISTORICAL DEVELOPMENT

The story of how people hit on the highly nonintuitive world picture of quantum mechanics, in which the physical state of a system is represented by an element in an abstract linear space and its observable properties by operators in the space, is fascinating and exceedingly complicated. The theory could not have been deduced from experiment, for the elements of the linear space are in principle not observable. It is also true that the theory did not arise from one person's great insight, as happened in Einstein's discovery of general relativity theory. The much greater change from the classical world picture of Newtonian mechanics and general relativity to the quantum world picture came in many steps taken by many people, often against the better judgment of participants.

The goal of this chapter is to show how classical physicists could have hit on wave mechanics. The strategy is to select topics that still are (or ought to be) part of the fundamental lore of any modern physicist. There are three major elements in the story. The first is the experimental evidence that the energy of an isolated system can only assume special discrete or quantized values. The second is the idea that the energy is proportional to the frequency of a wave function associated with the system. (This is the famous de Broglie relation $E = h\nu$, for energy E and frequency ν). The third is the connection between the de Broglie relation and energy quantization through the mathematical result that a wave equation with fixed boundary conditions allows only discrete quantized values of the frequency of oscillation of the wave function (as in the fundamental and harmonics of the vibration of a violin string). Some substantial computations are presented in this chapter, but the physics is introduced piecemeal, as needed. The principles of wave mechanics are collected in the next chapter, and are generalized to an abstract linear space in chapter 3.

1 Energy Quantization and Heat Capacities

The Boltzmann Distribution

Consider an object—an atom, molecule, rock—in a mechanically stable state and well isolated from its surroundings. In classical or quantum theory the object has a definite energy, E, that is conserved. Also, if the object consists of several weakly coupled parts E is the sum of the energies of the parts. In classical mechanics, E can assume any value from some minimum to the maximum allowed by stability. In quantum theory the possible values of the energy are discrete, or quantized,

$$E = E_i, \quad i = 0, 1, 2, \ldots, \tag{1.1}$$

with E_0 the ground state energy, E_1 the energy in the first excited state, and so on. This remarkable quantization concept first appeared in 1900, in Planck's derivation of the blackbody radiation spectrum, as described in section 2. We will consider first the relevance of energy quantization to heat capacities of material objects, because the analysis is a little less lengthy.

To describe what happens when an object is heated to a given temperature T, let us imagine we have a statistical ensemble of $M \gg 1$ mechanically identical copies of the object, each of which has been placed in contact with a heat reservoir at temperature T, allowed to come to equilibrium, and then isolated. The reservoir is a macroscopic body much larger than the object. The ensemble might literally be a collection of objects, such as a large number of nearly free atoms, or we can think of the ensemble as representing one almost isolated object that is sampled at widely separated times.

The accidents of interaction of each object with the enormous number of atoms in the reservoir determine the probability distribution of final energies of the objects in the ensemble. Let N_i be the number of the M objects that are found to be in the i^{th} energy level. Then in the limit $M \to \infty$ the probability of finding that a randomly chosen object from the ensemble is in level i is defined to

$$P_i = N_i/M. \tag{1.2}$$

The value of M is required to suppress sampling fluctuations. If the ensemble represents one object sampled at many different times, P_i is the probability that the object observed at a randomly chosen time is found to be in level i.

It will be assumed that the probability P_i in equation (1.2) depends only on the temperature T of the reservoir and on the energy E_i of the object (or more generally on the conserved quantities, which could include particle number), so at fixed temperature T the probability P_i is some function of energy,

$$P_i = F(E_i). \tag{1.3}$$

This assumption is justified below, in section 26 on measurement theory. For now the problem is to find the function $F(E_i)$.

Suppose the object consists of two weakly interacting parts, 1 and 2, so the allowed values of the energy of the object are of the form

$$E_i = E_a^1 + E_b^2, \tag{1.4}$$

for all combinations a, b of energy levels E_a^1 of part 1 and E_b^2 of part 2. The probability that part 1 is found to have energy E_a^1 is $P_a^1 = F(E_a^1)$, and part 2 has energy E_b^2 with probability $P_b^2 = F(E_b^2)$. Since the two parts are not interacting, the probability that one part has a given energy cannot depend on what the energy of the other part happens to be, that is, the parts are statistically independent. Since probabilities for independent events multiply, the probability that the object that consists of the two parts is in the energy level E_i in equation (1.4) is

$$P_i = P_a^1 P_b^2. \tag{1.5}$$

By equation (1.3) this is

$$F(E_a^1 + E_a^2) = F(E_a^1)F(E_b^2). \tag{1.6}$$

Since this equation is supposed to hold whatever the energies, we can write it as

$$F(E_a + E_b) = F(E_a)F(E_a), \tag{1.7}$$

for any values of E_a and E_b.

If it is not obvious that the solution to the functional equation (1.7) is an exponential, take the logarithm and differentiate with respect to E_a or E_b:

$$\frac{d}{dE_a} \log F(E) = \frac{1}{F(E)} \frac{dF}{dE} = \frac{1}{F(E_a)} \frac{dF}{dE_a} = \frac{1}{F(E_b)} \frac{dF}{dE_b} = -\beta, \tag{1.8}$$

The momentum is $p = m\dot{x} = m\,dx/dt$, with m the mass, so the kinetic energy is $p^2/2m$. The spring constant is K, and the potential energy is $Kx^2/2$. As is readily checked, the natural frequency of the oscillator is $\omega = (K/m)^{1/2}$ (units of radians per second) or $\nu = \omega/(2\pi)$ (units of cycles per second = Hertz).

As discussed in the next section and in section 37, an electromagnetic radiation field can be described as a set of simple harmonic oscillators, one for each mode of oscillation. In working through the theory of thermal blackbody radiation, Planck introduced the constraint, as an intermediate step in the calculation, that the energy of each oscillator is only allowed to assume the discrete values

$$E_n = nh\nu = n\hbar\omega, \qquad n = 0, 1, 2, \ldots. \tag{1.21}$$

(We will use h and $\hbar \equiv h/2\pi$, as convenient.) Planck's sensible plan was to take the limit $h \to 0$ at the end of the calculation, but he noticed that the predicted blackbody spectrum would agree with the measurements if instead he took h to be a nonzero constant,

$$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-27}\,\mathrm{erg\,s}. \tag{1.22}$$

The value quoted here is the modern result. The only other improvement to the energy spectrum (allowed values of the energy) of a simple harmonic oscillator is to replace the integers n with $n + 1/2$. The additive constant of course does not affect a heat capacity (which is the rate of change of mean energy with temperature).

Einstein proposed that Planck's quantization rule might apply to a material oscillator such as an atom oscillating about its equilibrium position in a solid. Let us see how that would affect the heat capacity.

With Planck's quantization rule (1.21), the partition function (eq. [1.14]) for a one-dimensional simple harmonic oscillator is

$$Z = \sum_0^\infty e^{-nh\nu/kT} = \sum A^n, \tag{1.23}$$

with $A = e^{-h\nu/kT} = e^{-\beta h\nu}$. The trick for evaluating this sum is to note that we can write it

$$\begin{aligned} Z &= 1 + A + A^2 + A^3 + \ldots \\ &= 1 + A[1 + A + A^2 + \ldots] \\ &= 1 + AZ. \end{aligned} \tag{1.24}$$

Thus we see that the sum is

$$Z = \frac{1}{1-A} = \frac{1}{1-e^{-\beta h\nu}} = \frac{1}{1-e^{-h\nu/kT}}. \tag{1.25}$$

Equation (1.19) gives the mean thermal energy,

$$U = \frac{d}{d\beta}\log(1-e^{-\beta h\nu}). \tag{1.26}$$

On differentiating this expression out we get

$$U = \frac{h\nu}{e^{h\nu/kT}-1}. \tag{1.27}$$

This is the wanted expression for the mean thermal energy of a one-dimensional simple harmonic oscillator with natural frequency ν at temperature T.

The classical limit is obtained at high temperature, $kT \gg h\nu$. When $h\nu/kT$ is small, the Taylor series expansion of the exponential in equation (1.27), keeping only the first nontrivial term, is

$$e^{h\nu/kT} \sim 1 + \frac{h\nu}{kT}. \tag{1.28}$$

This brings equation (1.27) to

$$U = kT. \tag{1.29}$$

The heat capacity in this limit is $C = dU/dT = k$. This is a special case of the classical energy equipartition theorem. The theorem says that for every quadratic term in position or momentum in the Hamiltonian there is a contribution $kT/2$ to the mean thermal energy of the system. There are two quadratic terms in equation (1.20), giving a net value of kT, which checks equation (1.29). Of course, a reasonable quantum theory must agree with classical physics in the high energy limit where we know classical physics works.

In the opposite low temperature limit, $kT \ll h\nu$, the mean energy in equation (1.27) is suppressed by the exponential in the denominator, as is the heat capacity. That is, Planck's energy quantization assumption in equation (1.21) leads to a characteristic temperature $T_c = h\nu/k$ for an oscillator with natural frequency ν. If the temperature is much larger than T_c the energy quantization is scarcely noticeable, and we see classical behavior. If the temperature is well below T_c the situation is decidedly nonclassical: the oscillator is forced to the ground state that has the minimum allowed value of the energy. As discussed next, a similar effect applies to the kinetic energy of tumbling of a molecule in a gas.

Heat Capacity of Molecular Hydrogen

From the energy equipartition theorem of classical statistical mechanics we would have expected that the mean thermal energy of a gas of N hydrogen molecules is

$$\begin{aligned} U = \frac{1}{2} NkT[&3 \text{ (for the kinetic energy of translation in 3 dimensions)} \\ &+ 2 \text{ (for rotation of the axis in two directions)} \\ &+ 2 \text{ (for vibration along the axis)} \\ &+ 1 \text{ (for rotation about the axis)}], \end{aligned} \tag{1.30}$$

plus maybe more for vibrations of the internal structures of the individual atoms.

At $T \lesssim 100\,\mathrm{K}$ the measured heat capacity is $dU/dT \sim 3Nk/2$, so the hydrogen molecules act like a gas of pointlike particles, the only energy being the kinetic energy of translation. Following the discussion of the simple harmonic oscillator, we conclude that the energy levels corresponding to the kinetic energy of translation are close together compared to kT at $T \sim 100\,\mathrm{K}$, so classical energy equipartion applies to the motions of the molecules, and that the energy levels corresponding to the other modes of motion in equation (1.30) are more broadly separated, so these modes are not appreciably excited at $T \sim 100\,\mathrm{K}$.

At $T \sim 200$ to $400\,\mathrm{K}$ the heat capacity of molecular hydrogen gas is close to $dU/dT \sim 5Nk/2$, which is that of a classical gas of rigid dumbbells (the first two lines of eq. [1.30]). This means the energy of the first rotationally excited state of the molecule exceeds that of the ground state by the amount

$$E_1 - E_0 \sim kT_R, \qquad T_R \sim 200\,\mathrm{K}. \tag{1.31}$$

The allowed values of angular momentum in quantum mechanics will be computed in section 17. A useful order of magnitude approximation is Bohr's assumption, that the rotationally excited states are spaced at increments of angular momentum equal to $\hbar$. (This is discussed in section 4 below.) Let us check that these numbers make sense.

If the hydrogen molecule has angular momentum $\hbar$ in the first rotationally excited state, and the moment of inertia of the molecule is I, then the kinetic energy of rotation in this state is

$$U_R = \frac{\hbar^2}{2I} \sim kT_R, \tag{1.32}$$

with $T_R \sim 200K$. The first equation is the classical expression for kinetic energy of rotation. The second equation with equation (1.11) for k and (1.22) for $\hbar$ gives $I \sim 2 \times 10^{-41}\,\mathrm{g\,cm^2}$. We are only interested in checking the orders of magnitude, so let us approximate the moment of inertia of the molecule as $I \sim m_p r^2$, where

$$m_p = 1.67 \times 10^{-24}\,\mathrm{g} \tag{1.33}$$

is the proton mass and r is the separation of the two protons in the molecule. That gives $r \sim 3 \times 10^{-9}\,\mathrm{cm} = 0.3\,\mathrm{Å}$. The size of a hydrogen atom is set by the Bohr radius (eq. [4.9] below). Our result is about half a Bohr radius, reasonably close considering the rough approximations.

At $T \sim 2000\,\mathrm{K}$ the heat capacity approaches that of a classical gas of dumbbells each of which can vibrate in length. This means the first vibrationally excited state of the molecule has energy roughly an order of magnitude above the first rotationally excited state. At $T \sim 3000\,\mathrm{K}$ the gas dissociates into atomic hydrogen.

Einstein and Debye Solids

A solid stores energy in the vibrations of the atoms about their equilibrium positions. In the simplest approximation, which Einstein considered, each atom vibrates with the same frequency, ν, in each of three dimensions, so a solid containing N atoms can be thought of as $3N$ one-dimensional simple harmonic oscillators. The thermal energy of the solid is then, by equation (1.27),

$$U = \frac{3Nh\nu}{e^{h\nu/kT} - 1}. \tag{1.34}$$

The high temperature limit is $U = 3NkT$, as in equations (1.28) and (1.29), so the heat capacity at high temperature is the classical energy equipartition expression

$$C = \frac{\partial U}{\partial T} = 3Nk. \tag{1.35}$$

By 1900 it was known that equation (1.35) is a good approximation to the heat capacities of solids at room temperature (this is the empirical law of Dulong and Petit), but Nernst had found that the heat capacity drops well below this value at low temperature, approaching zero at $T \to 0$. Einstein (1907) showed how the energy quantization assumption allows us to understand the decrease of heat capacity at low temperature: the heat capacity in equation (1.34) is strongly suppressed at $T \ll h\nu/k$.

Though the Einstein model gives the right qualitative picture, it says the heat capacity goes to zero at low temperature much faster than the measurements. It is easy to see why. When an atom moves it can bring its neighbors with it. This lowers the restoring force, which greatly lowers the frequency. That is, a solid acts like a collection of oscillators with a wide range of different frequencies. The lower frequency modes of oscillation are thermally excited at lower temperatures, so the heat capacity varies more slowly with temperature than it would if all the frequencies were the same. The Debye model to be discussed next approximates the low frequency modes of vibration of the solid as sound or pressure waves. The computation is lengthy but worth knowing, because it is used not only here but in the theory of blackbody radiation (section 2) and radiative transitions (section 37).

The low frequency modes that can be excited at low temperatures have long wavelengths and so are not much affected by the fact that the mass is in discrete lumps, in the atoms. For these long wavelength modes it is a good approximation to treat the solid as a continuous fluid, with smoothly varying mass density $\rho(\mathbf{r}, t)$ and velocity $\mathbf{v}(\mathbf{r}, t)$.

The mass and velocity functions obey two equations that express mass conservation and momentum conservation. The former is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0, \tag{1.36}$$

while Newton's law $\mathbf{F} = m\mathbf{a}$ generalizes for a fluid to

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{v} = -\nabla P/\rho. \tag{1.37}$$

as **r**, or by its components, as $\mathbf{r} = (x, y, z)$, or by the index notation r_α with $r_1 = x$, $r_2 = y$, and $r_3 = z$.)

Equations (1.46) to (1.48) describe the normal modes of pressure oscillations of the solid in the fluid model, which we have noted is a good approximation at low temperatures where only the low frequency long wavelength modes are excited. (In a normal mode each mass element vibrates with the same frequency, as in eq. [1.46]. The word normal refers to the orthogonality relations discussed in section 12.) Since each mode behaves as a simple harmonic oscillator, we will follow Planck and Einstein in assuming that the allowed values of the energy of each mode are quantized, $E = h\nu = \hbar\omega$, where ω is the classical frequency of vibration of the mode (eq. [1.21]). (This assumption is justified in section 12 below.) Then at temperature T the mean thermal energy of the solid is given by equation (1.27):

$$U = \sum_{n_\alpha \geq 0} \frac{\hbar\omega_{\mathbf{n}}}{e^{\hbar\omega_{\mathbf{n}}/kT} - 1}. \tag{1.49}$$

The sum is over the triplets of nonnegative integers, with $\omega_{\mathbf{n}}$ given by equations (1.47) and (1.48),

$$\omega_{\mathbf{n}} = \frac{\pi c_s}{L}(n_x^2 + n_y^2 + n_z^2)^{1/2}. \tag{1.50}$$

The sum in equation (1.49) can be approximated by an integral, as follows. Let us write the change in k_α in equation (1.48) when n_α is incremented by unity, to $n_\alpha + 1$, as

$$\Delta k_\alpha = \frac{\pi}{L}. \tag{1.51}$$

Then we can write the sum over n_α as

$$\sum_{n_\alpha} = \frac{L}{\pi} \sum \Delta k_\alpha \sim \frac{L}{\pi} \int_0^\infty dk_\alpha. \tag{1.52}$$

The last step is a good approximation if the temperature is not exceedingly low, so that the sum extends to large n_α before the exponential in the denominator in equation (1.49) becomes large. In this case the fractional increment in k_α on each increment of n_α is small, so the sum is well approximated as an integral.

In three dimensions, equation (1.52) generalizes to

$$\sum = \frac{L^3}{\pi^3} \int_{k_\alpha > 0} d^3k. \tag{1.53}$$

At this point it is convenient to introduce new and even simpler boundary conditions. If the thermal energy is dominated by modes with wavelengths much shorter than the size of the solid, the heat capacity cannot depend on the shape of the object—we just have to specify some shape in order to fix definite boundary conditions for the wave equation. Mathematically convenient boundary conditions are that the solid fills a space periodic in a cube of width L, volume $V = L^3$, so the point (x, y, z) is the same as the point $(x + L, y, z)$ and so on for the other three directions. We can write solutions to the wave equation that satisfy these periodic boundary conditions as the real part of

$$\delta \propto e^{i\mathbf{k}\cdot\mathbf{r}-\omega t}, \qquad \omega = kc_s. \tag{1.54}$$

The periodic boundary condition is that δ cannot change if x is shifted to $x + L$, so the propagation vector $\mathbf{k}$ has to satisfy

$$k_\alpha = \frac{2\pi n_\alpha}{L} \quad \text{or} \quad \mathbf{k} = \frac{2\pi \mathbf{n}}{L}. \tag{1.55}$$

Here $\mathbf{n}$ means the triplet of integers n_α of either sign,

$$n_\alpha = 0, \pm 1, \pm 2, \ldots. \tag{1.56}$$

Note that in the standing wave solution in equation (1.46) negative and positive integers (which means negative and positive k_α) are physically equivalent, the only difference being a change of sign which can be absorbed in the phase ϕ. Equation (1.54) represents a running wave, so a change of sign of n_α means a change in the direction the wave is running, which is a physical difference. Thus here we must sum over all eight octants of $\mathbf{n}$, while the sum in equation (1.53) is over the first octant only. A second difference is that here the increment in k_α for a unit increment of n_α is, by equation (1.55),

$$\Delta k_\alpha = \frac{2\pi}{L}, \tag{1.57}$$

twice the value in equation (1.51). Thus with periodic boundary conditions the sum over modes is approximated as the integral

$$\sum_{\mathbf{n}} = \frac{V}{(2\pi)^3} \int d^3k. \tag{1.58}$$

The integral is over all octants, 8 times the volume of the integral over the first octant in equation (1.53). This cancels the extra factor 2^3 in the denominator in equation (1.58).

Collecting equations (1.49) and (1.58), we see that the thermal energy of the solid is

$$U = \frac{V}{(2\pi)^3} \int d^3k \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}. \tag{1.59}$$

Because of the appearance of the factor V from the conversion of the sum to an integral, this equation says the energy per unit volume, U/V, is independent of the volume of the solid, which makes sense.

Since the integrand in equation (1.59) depends only on the magnitude of $\mathbf{k}$, we can write the volume element as $d^3k = 4\pi k^2 dk$. Then with $\omega = kc_s$ (eq. [1.54]) and the change of variables

$$y = \frac{\hbar\omega}{kT}, \tag{1.60}$$

(and taking care not to confuse Boltzmann's constant and the magnitude of the propagation vector) we get

$$U = \frac{V(kT)^4}{2\pi^2(\hbar c_s)^3} \int_0^\infty \frac{y^3 dy}{e^y - 1}. \tag{1.61}$$

The dimensionless integral is

$$\int_0^\infty \frac{y^3 dy}{e^y - 1} = \frac{\pi^4}{15}. \tag{1.62}$$

The final step is to note that energy can be stored also in shear waves, of which there are two for every pressure wave (shear in the two orthogonal directions perpendicular to the propagation vector $\mathbf{k}$), so we should multiply U by three and replace c_s with a mean velocity c_o

suitably averaged over pressure and shear modes. This gives the Debye equation,

$$\frac{U}{V} = \frac{\pi^2}{10}\frac{(kT)^4}{(\hbar c_o)^3}. \tag{1.63}$$

It will be recalled that this equation applies at low temperature where only long wavelength modes are excited. It gives a good approximation to the low temperature heat capacity of many solids. In others there are significant additional contributions, such as from thermal motions of electrons.

2 Blackbody Radiation

What Was Known in 1900

Consider a black cavity with walls at temperature T and a small hole to let us sample the radiation it contains. "Black" means that any light that enters the hole from outside is absorbed; any radiation coming out was emitted by the walls. At thermal equilibrium, the radiation energy with frequency in the range ω to $\omega + d\omega$ found in the volume element dV in the cavity is

$$du = u_\omega dV d\omega. \tag{2.1}$$

As indicated, the energy has to be proportional to the size dV of the volume element and to the bandwidth $d\omega$. The constant of proportionality, u_ω, is the spectral energy density, the energy per unit volume and unit bandwidth.

The second law of thermodynamics says u_ω can only depend on ω and on the wall temperature, T, independent of the nature of the wall. For we can imagine connecting two cavities made of different materials at the same temperature by a light pipe that passes only frequencies in the range ω to $\omega + d\omega$. If the radiation energy densities were different in the two cavities, we would find that heat is moving spontaneously from one reservoir to another at the same temperature, which alas is forbidden by the second law.

The net energy density is

$$u = \int_0^\infty u_\omega d\omega = aT^4. \tag{2.2}$$

This T^4 law was found empirically by Stefan (1879) and derived (apart from the value of Stefan's constant, a) by Boltzmann (1884) from thermodynamics.

A Quick Review of Electromagnetism

As a first step in the derivation of u_ω, let us write down Maxwell's equations. We will use Gaussian cgs units, where the electric and magnetic fields satisfy

$$\begin{aligned} &\nabla \cdot \mathbf{E} = 4\pi\rho, \qquad \nabla \cdot \mathbf{B} = 0, \\ &\nabla \times \mathbf{E} + \frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} = 0, \\ &\nabla \times \mathbf{B} - \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c}\mathbf{j}. \end{aligned} \tag{2.3}$$

The charge density is ρ, and the charge conservation equation is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0, \tag{2.4}$$

where $\mathbf{j}$ is the current density. This can be compared to equation (1.36) for mass conservation. The force on a charge q moving at velocity $\mathbf{v}$ is

$$\mathbf{F} = q\,(\mathbf{E} + \mathbf{v} \times \mathbf{B}/c). \tag{2.5}$$

The charge is measured in electrostatic units, where the static electric field at position $\mathbf{r}$ relative to a point charge q is

$$\mathbf{E} = \frac{q\mathbf{r}}{r^3}. \tag{2.6}$$

The electric and magnetic fields have the same units; for $\mathbf{B}$ the unit is called a Gauss. The velocity of light is c.

To get the electromagnetic wave equation we need the identity

$$\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B}). \tag{2.7}$$

This also applies to the gradient operator and a vector function of position, as long as we are careful not to change the order of differentiation. Thus we find from equation (2.7)

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2\mathbf{E}. \tag{2.8}$$

temperature, and the velocity of light c, Planck could solve for Boltzmann's constant k and $\hbar$; both were within 2 percent of the modern values.

Planck emphasized that, if his approach has any validity, $\hbar$ ought to show up somewhere else in physics. Einstein gave the first two examples: heat capacities, as discussed in the last section, and the photoelectric effect to be discussed next.

3 Photons

Light shining on a metal knocks out electrons. Einstein (1905) proposed an interpretation of this effect based on Planck's prescription $E = n\hbar\omega$ (eq. [1.21]) for the energy of an oscillator. Planck's prescription indicates that light can only transfer energy in discrete units—photons, or quanta of the electromagnetic field—of amount $\hbar\omega$. If one of these units of energy is given to an electron in a metal, then the electron ought to leave the metal with energy

$$E \leq \hbar\omega - \Phi, \tag{3.1}$$

where Φ is the binding energy (the work required to pull an electron out of the metal). The inequality takes account of the fact that the electron may lose energy before reaching the surface. By 1917, Millikan had found that there is a linear relation between the maximum energy of the electrons released and the frequency of the incident light, consistent with equation (3.1), and had found that the slope $\hbar$ of the relation agrees with Planck's value within the errors, again about 1 percent.

As discussed in chapter 8, the relativistic relation between the energy E of a particle, its momentum p, and its rest mass m is

$$E^2 = p^2c^2 + m^2c^4. \tag{3.2}$$

If the energy in light acts as discrete units, photons, perhaps the photons move as particles. Because these particles would have to move at the velocity of light, their rest mass would have to vanish, $m = 0$. The relativistic relation (3.2) indicates $E = pc$ for massless particles. Thus a photon with energy $E = \hbar\omega$ would be expected to have momentum

$$p = E/c = \hbar\omega/c. \tag{3.3}$$

Einstein was cautious about referring to the momentum of a photon; that it really has momentum in agreement with this equation was made clear by the Compton effect, that refers to the recoil of an electron that scatters a photon, as follows.

Imagine a photon of energy pc and momentum $\mathbf{p}$ incident on an electron of mass m that initially is at rest. The net energy and momentum of the system are therefore $E = pc + mc^2$ and $\mathbf{p}$. If the photon scatters off the electron and leaves with momentum $\mathbf{p}'$, then to conserve momentum the electron must end up with momentum $\mathbf{P} = \mathbf{p} - \mathbf{p}'$. The final energy, which must be the same as the initial, is

$$E = pc + mc^2 = p'c + [(\mathbf{p} - \mathbf{p}')^2 c^2 + m^2 c^4]^{1/2}. \tag{3.4}$$

On subtracting $p'c$, squaring, and simplifying we get

$$p' = \frac{mcp}{mc + p - p\cos\theta}, \tag{3.5}$$

where θ is the angle between $\mathbf{p}$ and $\mathbf{p}'$.

Using equation (3.3), we can write equation (3.5) as a relation between the initial and final frequencies ω and ω' of the photon,

$$\frac{1}{\omega'} = \frac{1}{\omega} + \frac{\hbar}{mc^2}(1 - \cos\theta). \tag{3.6}$$

Compton experimentally found this relation between the initial and final frequencies and the scattering angle, θ. This shows that light does scatter like a gas of massless particles, photons, with the usual relation (3.2) between energy and momentum.

4 Spectra and Energy Quantization of Atoms

The Combination Principle

A hot dilute gas of atoms or molecules emits light at sharply defined frequencies, ν_i. The set of values of these frequencies for a given material can be written as differences among a list of quantities called terms:

$$\nu_i = T_\alpha - T_\beta. \tag{4.1}$$