Grey Alien Transcript: Bohm Quantum Theory Chapter 1

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Bonjour tout le monde. Today's video going to be doing a partial review of Quantum Theory by David Bohm.

This is a special book because Bohm est la nom de guerre donné à l'interpretation de la théorie quantique par les Hidden Variables.

But in this book as will be discussed here, Bohm develops the so-called Copenhagen interpretation à la Bohr and Heisenberg,
and in this text, Bohm is actually critical of Hidden Variables.

Like other physics books, a mathematician might say it's loosey-goosey in its math treatment,
however the book is unique in its philosophical perspective,
and its place in Time makes it an interesting touchstone in the development towards the current understanding.

The book has 6 parts which develop quantum theory not only through mathematical, abstract, theoretical arguments but closely along experimental lines.

Quantum Theory by David Bohm was originally published in 1951, that is to say before the dumpster fire known as the Standard Model of particle physics raged into the inferno it is today.

Extreme amounts of money had not yet been spent to build massive particle colliders in multinational efforts, and thus only the O.G. quantum experiments form the foundation of Bohm's presentation in the book.

To further understand what this means, it is worth briefly reviewing first the state of physics leading up to Bohm's book, as this is referred to as "classical" physics throughout the text.

Physics at the time of Bohm's writing in the early 1950s had already made tremendous relative progress in the understanding of mechanics, electromagnetism, thermodynamics, fluid dynamics, and optics.

The giants include Isaac Newton and James Clerk Maxwell, but a few other special mentions are worth making for the purposes here.

Christiaan Huygens, the inventor of pendulum clocks,
was a contemporary of Descartes and Fermat and would anticipate calculus by about a decade in his geometric studies.

Huygens authored the first modern work on mechanics, *Horologium Oscillatorium*, which idealizes a physical problem by a analyzing a set of mathematical parameters.

Huygens would also inaugurate the wave theory of light; however, this was overshadowed by Newton's corpuscular theory of light.

Newton is obviously a physics giant and still to this day, although Leibniz notation is the norm, physics problems often amount to posing and analyzing or solving a differential equation or system of differential equations using calculus.

In the wake of Newton, this sort of general mathematical approach helped motivate the rigorous development of the branch of mathematical analysis.

Figures such as Siméon Denis Poisson would develop mathematical formulations from physical ideas that would turn out to be incorrect, but the math would be vindicated.

Augustin-Jean Fresnel and Augustin-Louis Cauchy would independently refine math and physics to a point where a wave theory of light would result, thus supplanting Newton's corpuscular theory of light.

Figures such as Karl Weierstrass would formalize mathematical analysis to give calculus the rigorous underpinning necessary to make increasingly precise statements in applications including physics.

Weierstrass' rigor enables the modern treatment of expressions such as Poisson's equation or the system of differential equations governing electromagnetism named after the giant in his own right, James Clerk Maxwell.

In the scope of Bohm's *Quantum Theory*, thermodynamics around Maxwell's time is worth exploring briefly before getting into the book.

Before Maxwell came Otto von Guericke who in 1650 was motivated to disprove Aristotle's supposition that "nature abhors a vacuum" and so he built the first known vacuum pump and demonstrated a vacuum, thus inaugurating modern thermodynamics.

Thermodynamics would culminate in the analysis of processes and systems in terms of their energy, entropy, volume, temperature, and pressure, and would be tangential to a deeper understanding of the nature of atoms and molecules.

Democritus' atomism would begin to be rigorously empirically validated around the turn of the nineteenth century through the findings of Joseph Proust and John Dalton in chemistry, which provided evidence that chemical elements combine with each other by basic units of weight.

Critically, by the late nineteenth century the reality of atoms and molecules was still disputed by philosophers and scientists alike opposed to the descriptions made by Maxwell, for example, as made in his paper *"Illustrations of the Dynamical Theory of Gases"*, and the overall kinetic theory of gases including the second law of thermodynamics developed by Ludwig Boltzmann.

Recall that thermodynamics in this era would originate two iconic philosophical thought experiments, namely Boltzmann brains and Maxwell's demon.

Both are related to a contemplation of the concept of entropy and the second law of thermodynamics which states that the entropy of an isolated system left to spontaneous evolution cannot decrease with time.

Max Planck, who will be discussed further shortly, once stated that *"The logarithmic connection between entropy and probability was first stated by Ludwig Boltzmann in his kinetic theory of gases."*

Entropy and the second law of thermodynamics are pillars of Boltzmann's statistical mechanics in their description of how macroscopic observations such as temperature and pressure are related to microscopic parameters that are described probabilistically.

A Boltzmann brain is the idea that it is probably more likely for a brain to spontaneously form, complete with a memory of having existed in the universe, rather than for the entire universe to come about in the manner cosmologists think it actually did.

Maxwell's demon directly confronts the second law of thermodynamics by aiming to directly disprove it.

Maxwell's demon controls a door between two chambers filled with gas, and as the individual gas particles approach the door, Maxwell's demon quickly opens and closes the door so as to only allow fast-moving particles in one chamber and only allow slow-moving particles into the other.

This would lead the kinetic temperature of one chamber to warm up and the other to cool down due to the actions of Maxwell's demon,
therefore, decreasing the total entropy of the system seemingly without applying any work,
and thus, violating the second law of thermodynamics.

Although the text is by no means organized in a strictly historical order, the discourse on physics presented in Bohm's book *Quantum Theory* begins with advances made around the turn of the twentieth century.

A major motivation for developing a deeper understanding of physics, namely thermodynamics, at the border of macroscopic and microscopic phenomena in this time, was the improvement of steam engine efficiency which was part of the main thrust of the ongoing industrial revolution.

Lord Kelvin was a player at the heart of the engine room of this drive towards greater thermodynamics understanding.

In a lecture he gave towards the end of his heyday in 1900 Lord Kelvin pronounced that two "dark clouds" loomed over physics at the time, specifically confusion from 1. the results of the Michelson-Morley experiment concerning how matter moves through the aether and 2. black-body radiation.

The fog of these clouds would lift to shed light on what are now pillars of modern physics—relativity and quantum theory.

The story goes that the foundation of modern physics in general is built upon the emergence of these fields and Einstein's four 1905 Annus mirabilis papers.

Each of these papers respectively covered the photoelectric effect, Brownian motion, special relativity, and mass-energy equivalence, all of which will be conceptually in the background of Bohm's *Quantum Theory* to various extents.

Everyone is now an expert in relativity and fluent in differential geometry, but appreciating the origins of Quantum Theory and the beginning of Bohm's book involves exploring the problem of Lord Kelvin's second cloud which led to the so-called "other pillar" of modern physics, namely black-body radiation.

The story of the exploration of black-body radiation is intertwined with the story of the exploration of the specific heat of a substance.

The common theme of these two explorations is the concept of thermal energy equilibrium.

Keep in mind that thermal equilibrium occurs when there is no net flow of thermal energy between connected systems, whereby the temperature is uniform and heat is not being exchanged.

Thermodynamic equilibrium is broader and requires that simultaneously there is thermal equilibrium, mechanical equilibrium (namely no pressure differences), and chemical equilibrium.

Black-body radiation is the thermal electromagnetic radiation in thermodynamic equilibrium within a black-body.

A black-body in Bohm's context is an idealized, perfectly-insulated hollow cavity.

The original radiant energy within the black-body continually emits waves of every possible frequency and direction at a rate which increases very rapidly with the temperature,
but this emission is opposed by the process of absorption in the walls taking place at a rate proportional to the intensity of radiation already present in the cavity.

Thus, the black-body and its internal radiation are in thermodynamic equilibrium.

To observe or measure this internal radiation, a hole is made in the wall of the black-body which is effectively small enough that there is a negligible effect upon the system's equilibrium.

The idea of a black-body goes back to Newton who stated in his work titled *Opticks* that
"Do not black Bodies conceive heat more easily from Light than those of other Colours do, by reason that the Light falling on them is not reflected outwards, but enters into the Bodies, and is often reflected and refracted within them, until it be stifled and lost?"

Augustin-Jean Fresnel would later respond by saying that a black body under illumination would increase indefinitely in heat.

This sort of back-and-forth is a debate surrounding the relationship between the energy and wavelength of electromagnetic radiation and/or light incident upon matter, the energy absorbed by the matter if any,
and the energy and wavelength of the electromagnetic radiation and/or light subsequently emitted by the matter as a result.

To assess the validity of such purported truths and the extent that they apply in nature, theoretical and experimental approaches were taken.

Begin with the system of partial differential equations that are Maxwell's Equations, namely Gauss's law, Gauss's law for magnetism, Faraday's law, and the Ampère-Maxwell law.

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$
$$\nabla \times \mathbf{B} = \mu_0 \left(\mathbf{J} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right)$$

The black-body cavity contains energy in the form of electromagnetic radiation, so determine the energy distribution among the frequencies in the cavity when the walls are at a given temperature.

The periodic nature of these waves in terms of the contributions of various frequencies lends itself to a solution via the series expansion in terms of orthogonal functions, i.e., a Fourier Analysis.

Thus, the radiation behaves like a collection of simple harmonic oscillators called *"radiation oscillators"* which can be given a classic statistical mechanical treatment that yields the mean energy of each oscillator at equilibrium with the black-body walls at a temperature T.

This enables the determination of the number of oscillators in a given frequency, which when multiplied by the mean oscillator energy yields a thermodynamic result known as the Rayleigh-Jeans law.

General electric and magnetic fields are given through Maxwell's Equations in terms of vector and scalar potentials, say $\mathbf{a}$ and ϕ, namely in Bohm's notation

$$\mathcal{H} = \nabla \times \mathbf{a} \quad \text{and} \quad \mathcal{E} = -\frac{1}{c}\frac{\partial \mathbf{a}}{\partial t} - \nabla \phi$$

These solutions of Maxwell's Equations are not unique and so an arbitrary scaling which maps $(\mathbf{a},\ \phi) \rightarrow (\mathbf{a}', \phi')$ can be introduced that leaves the magnetic field $\mathcal{H}$ and $\mathcal{E}$ unchanged.

These scalings are
$\nabla\psi$ subtracted from the vector potential $\mathbf{a}$ since this leaves $\mathcal{H}$ unchanged, i.e., $\nabla \times \nabla\psi = 0$
and $\frac{1}{c}\frac{\partial}{\partial t}\psi$ added to the scalar potential ϕ since this leaves $\mathcal{E}$ unchanged.

Thus, one has that $\mathbf{a}' = \mathbf{a} - \nabla\psi$ and $\phi' = \phi + \frac{1}{c}\frac{\partial\psi}{\partial t}$.

Additionally, imposing the condition that $\nabla \cdot \mathbf{a} = 0$ completes making a transformation called the Coulomb gauge fixing.

The Coulomb gauge, also known as the transverse of radiation gauge, is a gauge-fixing condition specifically defined by this setting of the divergence of the vector potential to zero.

This is useful in non-relativistic quantum electrodynamics and for bound or stationary states in that it eliminates non-physical degrees of freedom, allowing for a natural Hamiltonian formulation and instantaneous longitudinal interactions.

Recall that the Hamiltonian of a system refers to an operator corresponding to the total energy of that system, namely the combined kinetic energy and potential energy, denoted as $\hat{H} = \hat{T} + \hat{V}$.

This gauge fixing condition is thus sometimes referred to as the transverse gauge because it ensures that the vector potential is purely transverse.

In Quantum Electrodynamics, eliminating non-physical degrees of freedom amounts to isolating physical photons, namely their transverse components, and furthermore the Coulomb gauge separates the longitudinal Coulomb potential from the radiation field.

The advantage is that this directly shows the electrostatic potential or the static Coulomb interaction as the scalar potential,
but the disadvantage is that it is not a relativistic gauge fixing condition such as the Lorentz gauge, i.e., $\nabla \cdot \mathbf{a} + \frac{1}{c^2}\frac{\partial V}{\partial t} = 0$ which *is* Lorentz invariant.

After imposing the Coulomb gauge condition that $\nabla \cdot a = 0$, the invariance of fields serves the purpose of simplifying the previously obtained scaled expressions for $\mathcal{E}$ and $\mathcal{H}$.

This requires calculating a new expression for $\nabla \cdot \mathbf{a}'$, or in other words, ψ must be chosen such that $\nabla \cdot \mathbf{a} - \nabla^2 \psi = 0$.

Recognize that what is being sought is the solution of Poisson's equation.

ψ is thus the solution of the potential field in Poisson's equation from the source density given by $\nabla \cdot \mathbf{a}'$.

The general representation of this solution is given by

$$\psi = -\frac{1}{4\pi} \int\int\int \frac{\nabla \cdot \mathbf{a}(x', y', z', t) \mathrm{d}x' \ \mathrm{d}y' \ \mathrm{d}z'}{|\mathbf{r} - \mathbf{r}'|}$$

The formulation of this general representation demonstrates that a Coulomb gauge transformation that yields $\nabla \cdot \mathbf{a}'$ can always be calculated.

The physical formulation of the problem can be followed to further simplify the previous general expressions for the $\mathcal{E}$ and $\mathcal{H}$ fields.

The black-body cavity by hypothesis does not contain any charges and is therefore empty space.

The choice that $\nabla \cdot \mathbf{a} = 0$ also leads to $\phi = 0$.

This can be seen by substituting $\mathcal{E} = -\frac{1}{c}\frac{\partial \mathbf{a}}{\partial t} - \nabla\phi$ into Gauss's law, namely

$$\nabla \cdot \mathcal{E} = -\frac{1}{c}\nabla \cdot \frac{\partial \mathbf{a}}{\partial t} - \nabla^2\phi = 0$$
$$\text{then,} \quad \nabla \cdot \mathbf{a} = 0 \Rightarrow \nabla^2\phi = 0$$

This is Laplace's equation.

Therefore, an analytic deduction by the regularity of Laplace's equation from its algebraic structure indicates that the only solution of this equation over all of space is $\phi = 0$.

Otherwise, nonzero regular solutions could only occur provided that the charge density ρ is not everywhere zero, and thus relevant solutions of Poisson's equations would be sought.

Therefore, the $\mathcal{E}$ and $\mathcal{H}$ field expressions subject to $\nabla \cdot \mathbf{a}$ in the absence of charges are given by

$$\mathcal{H} = \nabla \times \mathbf{a}$$
$$\mathcal{E} = -\frac{1}{c}\frac{\partial \mathbf{a}}{\partial t}.$$

The physical formulation of the black-body cavity additionally hypothesizes zero charge density therein, so substituting the foregoing expressions for the $\mathcal{E}$ and $\mathcal{H}$ fields into the Ampère-Maxwell law obtains the partial differential equation

$$\nabla^2 \mathbf{a} - \frac{1}{c^2}\frac{\partial^2 \mathbf{a}}{\partial t^2} = 0$$

The next step is to specify the boundary conditions to obtain an appropriate solution for this partial differential equation.

The theoretical black-body cavity can be idealized by first considering a cube of side length L with very thin, non-conductive walls repeated periodically through the space in all directions and thereby the radiation fields are the same at corresponding points of every internal cube.

These idealized walls being thin and non-conductive serves to prevent the system from gaining or losing energy.

This motivates seeking a solution in terms of periodic fields, which achieves the same effect as such theoretical very thin, non-conductive walls because each cube can't gain nor lose energy from the other cubes and thus the energy in any single cube is constant.

Since the walls of the black-body cavity are absorbing and emitting radiation in thermodynamic equilibrium, the sole restriction imposed on Maxwell's equations in this situation is that the solution $\mathbf{a}(x, y, z, t)$ is periodic in space with a period L/n where n is an integer.

This scenario lends itself to employing a Fourier Analysis where a partial differential equation is transformed into an ordinary differential equation or an algebraic equation with fewer variables.

Furthermore, the expansion of the solution in terms of a basis of orthogonal functions such as sines and cosines is conducive to representing periodic solutions.

In the context of black-body radiation, an arbitrary f is sought here as a sum of standing waves of all possible wavelengths and amplitudes.

There are a handful of variations of expressing Fourier Series but the representation given in Bohm's *Quantum Theory* is to write the function f as

$$f(x,y,z,t) = \sum_{l,m,n} \left[a_{l,m,n}(t) \cos \frac{2\pi}{L}(lx + my + nx) + b_{l,m,n}(t) \sin \frac{2\pi}{L}(lx + my + nz) \right]$$

for integers l, m, and n from $-\infty$ to ∞ including 0.

Convergent a and b coefficients thus define a periodic f.

These coefficients were expressed in Bohm's book through the relations

$$a_{l,m,n}(t) + a_{-l,-m,-n}(t) = \frac{1}{L^3} \int_0^L \int_0^L \int_0^L \mathrm{d}x \; \mathrm{d}y \; \mathrm{d}z \;\; \cos \frac{2\pi}{L}(lx + my + nz) f(x,y,z,t)$$
$$b_{l,m,n}(t) - b_{-l,-m,-n}(t) = \frac{1}{L^3} \int_0^L \int_0^L \int_0^L \mathrm{d}x \; \mathrm{d}y \; \mathrm{d}z \;\; \sin \frac{2\pi}{L}(lx + my + nz) f(x,y,z,t)$$

and as such, f is specified only by $a_{l,m,n}$ and $b_{l,m,n}$.

Notably this involves the following orthogonality relations:

$$\int_0^L \int_0^L \int_0^L \mathrm{d}x \ \mathrm{d}y \ \mathrm{d}z \ \cos\frac{2\pi}{L}(lx+my+nz)\sin\frac{2\pi}{L}(l'x+m'y+n'z) = 0$$
$$\int_0^L \int_0^L \int_0^L \mathrm{d}x \ \mathrm{d}y \ \mathrm{d}z \ \cos\frac{2\pi}{L}(lx+my+nz)\cos\frac{2\pi}{L}(l'x+m'y+n'z) = 0$$

which hold unless $\begin{pmatrix} l & = l' \\ m & = m' \\ n & = n' \end{pmatrix}$ or $\begin{pmatrix} l & = -l' \\ m & = -m' \\ n & = -n' \end{pmatrix}$ and therefore each coordinate equals $\frac{L^3}{2}$, or otherwise when $l = m = n = 0$ then each coordinate therefore equals L^3.

Similarly,

$$\int_0^L \int_0^L \int_0^L \mathrm{d}x \ \mathrm{d}y \ \mathrm{d}z \ \sin\frac{2\pi}{L}(lx+my+nz)\sin\frac{2\pi}{L}(l'x+m'y+n'z) = 0$$

which is subject to the same caveat as previously for the coordinates l, m, and n for the other orthogonality relations.

Using these expressions and relations, the vector potential can now be expanded in a Fourier Series.

Since the solution a has been formulated as a vector with 3 components, the Fourier coefficients $a_{l,m,n}$ and $b_{l,m,n}$ likewise have 3 components.

$$\Rightarrow \mathbf{a} = \sum_{l,m,n} \left[a_{l,m,n}(t)\cos\frac{2\pi}{L}(lx+my+nz) + b_{l,m,n}\sin\frac{2\pi}{L}(lx+my+nz) \right]$$

Assume that the offset $a_{0,0,0} = 0$.

At this point, Bohm defines a propagation vector $\mathbf{k}$ via

$$k_x = \frac{2\pi l}{L}, \ k_y = \frac{2\pi m}{L}, \ k_z = \frac{2\pi n}{L}, \ k^2 = (\frac{2\pi}{L})^2(l^2+m^2+n^2) \qquad (1)$$

Next, the coordinate axis is oriented so that the z-axis is along $\mathbf{k}$, thus $l = m = 0$, $k = \frac{2\pi}{L}$.

The definition of k implies that $\frac{k}{2\pi}$ is the number of waves in the distance L.

In other words, the wavelength is $\lambda = \frac{2\pi}{k}$ which is equivalent to saying that $k = \frac{2\pi}{\lambda}$, which implies that $\mathbf{k}$ is in the direction that the phase of the wave changes.

Changing back to arbitrary coordinate axes implies that $\mathbf{k}$ is in the direction of the wave's propagation magnitude, $\frac{2\pi}{\lambda}$,
and is allowed to take on the values permitted by integral values of l, m, and n per the previous definitions (1).

Accumulating these results and simplifying the notation yields

$$\mathbf{a} = \sum_k \left[a_k(t)\cos\mathbf{k}\cdot\mathbf{r} + b_k \sin\mathbf{k}\cdot\mathbf{r}\right] \tag{2}$$

where the sum is over all permissible values of k.

Applying $\nabla \cdot \mathbf{a} = 0$ to (2) yields

$$\mathbf{a} = \sum_k \left[-\mathbf{k}\cdot\mathbf{a}_k \sin\mathbf{k}\cdot\mathbf{r} + \mathbf{k}\cdot\mathbf{b}_k \cos\mathbf{k}\cdot\mathbf{r}\right] = 0.$$

By the previous orthogonality relation, if a Fourier series sums to 0, then all coefficients a_k and b_k must vanish.

Therefore, $\mathbf{k}\cdot\mathbf{a}_k(t) = \mathbf{k}\cdot\mathbf{b}_k = 0$, and this $\mathbf{a}_k$ and $\mathbf{b}_k$ are orthogonal to $\mathbf{k}$, as are the $\mathcal{E}$ and $\mathcal{H}$ fields of the k^{th} wave.

Vibrations are also normal to the propagation direction, and therefore the waves are transverse.

The direction of the $\mathcal{E}$ field is referred to as the "direction of polarization".

Return to the coordinate axes where the z-axis is in the direction of $\mathbf{k}$ to describe the orientation of $\mathbf{a}_k$.

$\mathbf{a}_k$ only has x and y components, therefore specifying these also specifies the magnitude and direction of $\mathbf{a}_k$.

Thus, designate the direction of $\mathbf{a}_k$ by the polarization index μ, and write $\mathbf{a}_{k,\mu}$ such that $\mu = 1,\ 2$, i.e., $\mu = 1$ designates the x-direction, and $\mu = 2$ designates the y-direction.

All possible $\mathbf{a}_k$ vectors can be represented as the sum of some $\mathbf{a}_{k,1}$ and $\mathbf{a}_{k,2}$, therefore the most general vector potential subject to the initial condition $\nabla \cdot \mathbf{a} = 0$ is given by

$$\mathbf{a}(\mathbf{r}, t) = \sum_{\mathbf{k},\mu} [\mathbf{a}_{\mathbf{k},\mu}(t) \cos \mathbf{k} \cdot \mathbf{r} \ \cdot \ \mathbf{b}_{\mathbf{k},\mu}(t) \sin \mathbf{k} \cdot \mathbf{r}] \widehat{\epsilon}_{\mathbf{k},\mu}$$

where $\widehat{\epsilon}_{\mathbf{k},\mu}$ is perpendicular to $\mathbf{k}$ such that each mode $\mathbf{a}_{k,\mu}$ satisfies

$$\frac{\mathrm{d}^2 \mathbf{a}_{k,\mu}}{\mathrm{d}t^2} + k^2 c^2 \mathbf{a}_{k,\mu} = 0 \tag{3}$$

Note that this equivalently amounts to stating that the $\mathbf{a}_{\mathbf{k},\mu}$ terms oscillate with simple harmonic motion with an angular frequency $\omega = c|\mathbf{k}|$, which follows from the wave equation for $\mathbf{a}$.

The next step is to evaluate the electromagnetic energy in the volume of the black-body cavity.

The total energy in the matterless space due to the radiation is given by

$$E = \frac{1}{8\pi} \int (\mathcal{E}^2 + \mathcal{H}^2)\ \mathrm{d}\tau$$

This follows from the Poynting Theorem which states that the rate of energy transfer per unit volume from a region of space equals the rate of work done on the charge distribution in the region, plus the energy flux leaving that region.

Recall that the goal is to determine the energy distribution among the frequencies in the cavity when the walls of the black-body are at a given temperature.

Thus, the previous expression for the total energy in the cavity will be evaluated over a cube of side length L using the foregoing Fourier series result for $\mathbf{a}$.

First, the $\mathcal{E}$ field is given by

$$\mathcal{E} = -\frac{1}{c}\sum_{k,\mu}\left(\dot{\mathbf{a}}_{k,\mu}\cos\mathbf{k}\cdot\mathbf{r} + \dot{\mathbf{b}}_{k,\mu}\sin\mathbf{k}\cdot\mathbf{r}\right).$$

Next, the $\mathcal{H}$ field is given by

$$\mathcal{H} = \sum_{k,\mu}\left(-\mathbf{k}\times\mathbf{a}_{k,\mu}\sin\mathbf{k}\cdot\mathbf{r} + \mathbf{k}\times\mathbf{b}_{k,\mu}\cos\mathbf{k}\cdot\mathbf{r}\right).$$

Next, evaluating the expression for electromagnetic energy over a cube of side length L yields

$$\begin{aligned}\frac{1}{8\pi}\int\mathcal{E}^2\,\mathrm{d}\tau = \frac{1}{8\pi c^2}\sum_{k,\mu}\sum_{k',\mu'}\int_0^L\int_0^L\int_0^L \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z(&\dot{\mathbf{a}}_{k,\mu}\cdot\dot{\mathbf{a}}_{k',\mu'}\cos\mathbf{k}\cdot\mathbf{r}\cdot\cos\mathbf{k}'\cdot\mathbf{r}\\ &+\dot{\mathbf{b}}_{k,\mu}\cdot\dot{\mathbf{b}}_{k',\mu'}\sin\mathbf{k}\cdot\mathbf{r}\cdot\sin\mathbf{k}'\cdot\mathbf{r}\\ &+\dot{\mathbf{a}}_{k,\mu}\cdot\dot{\mathbf{b}}_{k',\mu'}\cos\mathbf{k}\cdot\mathbf{r}\cdot\sin\mathbf{k}'\cdot\mathbf{r}\\ &+\dot{\mathbf{b}}_{k,\mu}\cdot\dot{\mathbf{a}}_{k',\mu'}\sin\mathbf{k}\cdot\mathbf{r}\cdot\cos\mathbf{k}'\cdot\mathbf{r})\end{aligned} \tag{4}$$

All integrals vanish except when $\mathbf{k} = \mathbf{k}'$ and all terms involving $\dot{\mathbf{a}}_{k,\mu}\cdot\dot{\mathbf{b}}_{k,\mu'} = 0$.

Also, $\dot{\mathbf{a}}_{k,\mu}\cdot\dot{\mathbf{a}}_{k,\mu'} = 0$ unless $\mu = \mu'$.

Next, (4) reduces to

$$\int\frac{\mathcal{E}^2\,\mathrm{d}\tau}{8\pi} = \frac{L^3}{8\pi c^2}\sum_{k,\mu}\left[\frac{1}{2}(\dot{\mathbf{a}}_{k,\mu})^2 + \frac{1}{2}(\dot{\mathbf{b}}_{k,\mu})^2\right], \text{ and similarly}$$

$$\int\frac{\mathcal{H}^2\,\mathrm{d}\tau}{8\pi} = \frac{L^3}{8\pi}\sum_{k,\mu}\left[k^2\frac{1}{2}(\mathbf{a}_{k,\mu})^2 + \frac{1}{2}(\mathbf{b}_{k,\mu})^2\right]$$

Therefore, the electromagnetic energy in the cavity, where L^3 is denoted as V, is thus

$$E = \frac{V}{8\pi c^2} \sum_{k,\mu} \left\{ \frac{1}{2} \left[(\dot{\mathbf{a}}_{k,\mu})^2 + c^2 k^2 (\mathbf{a}_{k,\mu})^2 \right] + \frac{1}{2} \left[(\dot{\mathbf{b}}_{k,\mu})^2 + c^2 k^2 (\mathbf{b}_{k,\mu})^2 \right] \right\} \quad (5)$$

Two observations follow.

First, (5) is a sum of separate $\mathbf{a}_{k,\mu}$ and $\mathbf{b}_{k,\mu}$ terms, therefore different wavelengths and polarizations don't interact.

The energy of each propagation vector $\mathbf{k}$ and polarization direction μ is proportional only to the square of $\dot{\mathbf{a}}_{k,\mu}$ and $\mathbf{a}_{k,\mu}$, and likewise for the b coefficients.

Second, The energy of the a and b coefficients, respectively, has the same mathematical form of a simple harmonic oscillator,

i.e., a simple harmonic oscillator with effective mass m and angular frequency ω

has the energy $E = \frac{m}{2}(\dot{x}^2 + \omega^2 x^2)$,

and the effective mass given by $m = \frac{V}{8\pi c^2}$, and likewise angular frequency $\omega = kc$.

Therefore, the frequency denoted $f = \frac{\omega}{2\pi} = \frac{kc}{2\pi} = \frac{c}{\lambda}$, which is the same as an electromagnetic wave with wavelength λ.

Also, from the expression momentum for a simple harmonic oscillator $p = m\dot{x}$ that in the present context of the black-body radiation solution it follows that $\dot{p}_{k,\mu} = \frac{V}{8\pi c^2}\dot{\mathbf{a}}_{k,\mu}$.

Thus, the expression for the Hamiltonian of a simple harmonic oscillator $H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$ implies that in the present context the Hamiltonian is given by $H = \frac{8\pi c^2}{L^3}\frac{(\dot{p}_{k,\mu})^2}{2} + \frac{L^3}{8\pi}k^2\frac{(\mathbf{a}_{k,\mu})^2}{2}$, and likewise for $\mathbf{b}_{k,\mu}$.

The correct equations of motion are obtained form the Hamiltonian

$$\dot{\mathbf{a}}_{k,\mu} = \frac{\partial H}{\partial p_{k,\mu}},\ \dot{p}_{k,\mu} = -\frac{\partial H}{\partial \mathbf{a}_{k,\mu}}$$

This yields (3) which was originally obtained by direct substitution into Maxwell's equations.

Therefore,

$$\ddot{\mathbf{a}}_{k,\mu} + c^2 k^2 \mathbf{a}_{k,\mu} = 0$$

and similarly for the b coefficients.

$\mathbf{a}_{k,\mu}$ and $\mathbf{b}_{k,\mu}$ are thus analogous to the coordinates of separate non-interacting harmonic oscillators, and also may be regarded as the coordinates of the radiation field.

There exist as such a countable infinite number of coordinates via the possible values of k.

The previously calculated Fourier Series describes fields in continuous space via a discrete infinite number of coordinates.

For each k there are then 2 independent coordinates, namely $\mathbf{a}_{k,\mu} + \mathbf{a}_{-k,\mu}$ and $\mathbf{b}_{k,\mu} - \mathbf{b}_{-k,\mu}$.

The next step is to find the number of oscillators with frequencies between v and $v + \mathrm{d}v$.

Since $v = kc/2\pi$, this is equivalent to finding the number of oscillators between k and $k + \mathrm{d}k$.

Choose $\mathrm{d}k$ to be so small that no important physical quantity such as mean energy, for example, changes appreciably, but so large that very many radiation oscillators are included.

This choice is made because many so-called reasonable choices of k would entail a large number of waves inside the box.

By choosing $\mathrm{d}k$ in this way, the number of oscillators can be treated as virtually continuous and may be represented via a density function.

The task is thus to find the number of oscillators in the volume $\mathrm{d}k_x$, $\mathrm{d}k_y$, and $\mathrm{d}k_z$.

That there is one oscillator per unit cube of l, m, n space implies that the density in this space is 1.

The previous definitions for the propagation vector (1) are then used to transform to k-space, therefore writing $\delta N_1 = \mathrm{d}l\ \mathrm{d}m\ \mathrm{d}n = \mathrm{d}k_x\ \mathrm{d}k_y\ \mathrm{d}k_z$.

Next, adopt polar coordinates so that $k^2 = k_x^2 + k_y^2 + k_z^2$ transforms the element of volume as $k^2\ \mathrm{d}k\ \mathrm{d}\Omega$ where $\mathrm{d}\Omega$ is the element of solid angle.

Integrating over $\mathrm{d}\Omega$ leads to a new element of volume $4\pi k^2 \mathrm{d}k$, and therefore $\delta N_1 = \frac{4\pi V}{(2\pi)^3} k^3\ \mathrm{d}k$.

By writing $v = kc/2\pi$, the expression $\delta N_1 = 4\pi V \frac{v^2\ \mathrm{d}v}{c^3}$ is obtained, which gives the number of permissible values of k in the range v to $v + \mathrm{d}v$.

Recall that there are two independent coordinates for all k, namely the a and b coordinates, and commensurately two directions of polarization.

Therefore, the number of oscillators between v and $v + \mathrm{d}v$ is finally given by

$$\delta N = 2\delta N_1 = \frac{8\pi V}{c^3} v^2\ \mathrm{d}v \tag{6}$$

The final step in the derivation is to apply classical statistical mechanics to calculate the mean energy possessed by each oscillator at thermodynamic equilibrium with the black-body walls.

Such a treatment applies to all systems acting like material oscillators.

In canonical ensemble, the probability (including a normalization factor A) that a system with total energy E , that is both kinetic and potential energy, is in the phase space element $\mathrm{d}p\ \mathrm{d}q$ is given by

$$A\mathrm{e}^{-E/(\kappa T)}\mathrm{d}p\ \mathrm{d}q$$

with the requirement that as an expression of probability it holds that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} A\mathrm{e}^{E/\kappa T}\mathrm{d}p\ \mathrm{d}q = 1.$$

In the above, κ denotes the Boltzmann constant which is approximately 1.38×10^{-23} J/K which provides a proportionality factor between kinetic energy at the particle level to gaseous temperature.

Next, the energy E must be specified.

In the case of a perfect gas, energy would be given by $E = p^2/2m$ which leads to obtaining the Maxwell-Boltzmann distribution of velocities $A\mathrm{e}^{-p^2/(2m\kappa T)}\mathrm{d}p\,\mathrm{d}q.$

As here in the case for one harmonic oscillator, energy is rather given by $E = \frac{p^2}{2m} + m\omega^2\frac{q^2}{2}$.

Next, a change of variables is introduced, i.e., $p = \sqrt{2m}P$ and $q = \frac{Q}{\omega}\sqrt{\frac{2}{m}}$ which yields $E = P^2 + Q^2$.

Thus, the previous statement of total probability becomes

$$\frac{1}{A} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{e}^{-E/\kappa T}\frac{2}{\omega}\mathrm{d}P\ \mathrm{d}Q.$$

The probability that the system lies within the phase space between P to $P + \mathrm{d}P$ and Q to $Q + \mathrm{d}Q$ is then

$$dW(P,Q) = \frac{\mathrm{e}^{-(P^2+Q^2)/(\kappa T)}\mathrm{d}P\ \mathrm{d}Q}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{e}^{-(P^2+Q^2)/(\kappa T)}\mathrm{d}P\ \mathrm{d}Q}.$$

Next, make another change of variables to transform to polar coordinates R and ϕ in phase space where

$$P^2 + Q^2 = R^2 = E, \quad \text{or} \quad R \, \mathrm{d}R = \frac{\mathrm{d}E}{2}.$$

Solutions are sought in terms of R rather than ϕ, thus integration is taken over ϕ,
therefore the normalized probability that the energy lies between E and $E + \mathrm{d}E$ is given by

$$\bar{E} = \frac{\int_0^\infty E \mathrm{e}^{-E/(\kappa T)} \mathrm{d}E}{\int_0^\infty \mathrm{e}^{-E/(\kappa T)} \mathrm{d}E} = \kappa T \frac{\int_0^\infty \mathrm{e}^{-\epsilon} \epsilon \, \mathrm{d}\epsilon}{\int_0^\infty \mathrm{e}^{-\epsilon} \mathrm{d}\epsilon} = \kappa T \tag{7}$$

where ϵ denotes $E/\kappa T$.

The foregoing demonstration that the average energy of each oscillator is κT is an example of the equipartition theorem of energy.

The theorem of equipartition of energy simply states that the total energy, both kinetic *and* potential as critically per the case of harmonic oscillators, is shared equally among all of its independent parts *on the average* once the system has reached thermal equilibrium.

This is a more subtle statement than classic conservation of energy.

Collecting the results of (6) and (7) results in what is known as the Rayleigh-Jeans law:

$$U(v) \, \mathrm{d}v = \bar{E} \, \delta N = \frac{8\pi V}{c^3} \kappa T v^2 \, \mathrm{d}v. \tag{8}$$

Notice that this result is proportional to the square of frequency, v^2.

Large frequencies correspond to small wavelength, which in the case of electromagnetic radiation corresponds to the ultraviolet spectrum and above.

Therefore, the Rayleigh-Jeans law diverges towards infinity at increasingly high frequencies of radiation.

This is problematic because the corresponding empirical evidence at the time had already demonstrated that,
while the Rayleigh-Jeans law agreed with experimental results at low frequencies, at high frequencies the emission reached a maximum and then fell with frequency, i.e., the total energy emission is finite.

This is referred to as the ultraviolet catastrophe, and indicates a shortcoming of the equipartition theorem from classical thermodynamics.

A prevailing source of experimentally accessible black-body radiation at the time of these developments in the years shortly before the turn of the 20^{th} century was an exposed incandescent solid body serving as an approximation to black-body radiation.

The shortcoming of experimental approaches with such bodies is that they were mere approximations to the behavior of radiation in a theoretical black-body.

While perfect black bodes do not exist in nature, the departure of emitted radiation from an exposed incandescent solid body from the black-body spectrum obscures the empirical discernment of the true black-body spectrum.

Nevertheless, experimental work by Otto Lummer, Ferdinand Kurlbaum, Ernst Pringsheim, and Heinrich Rubens demonstrated a setup which led to progressively improved measurements approximating ideal black-body radiation to more fully characterize the black-body spectrum.

Lummer and Kurlbaum's design involved a platinum box divided by diaphragms and an interior blackened with iron oxide, or later with a mixture of chromium, nickel, and cobalt oxides.

With better experimental data, a notable improvement on describing black-body radiation would be put forth by Wilhelm Wien.

An abbreviated sketch of the derivation of Wien's approximation is as follows.

It is assumed that the wavelength of the black-body radiation is proportional to the square of its velocity.

Begin with energy density $\rho(\lambda, T) = F(\lambda)\mathrm{e}^{-a/(\lambda T)}$ and then use the Stefan-Boltzmann law to obtain

$$\int_0^\infty F(\lambda)\mathrm{e}^{-a/(\lambda T)}\mathrm{D}\lambda \;\propto\; T^4 \tag{9}$$

Next, define $y = a/(\lambda T)$ and write the expansion of $F(\lambda)$ as

$$\begin{aligned} F(\lambda) &= F(\frac{a}{yT}) \\ &= c_0 + c_1\frac{yT}{a} + c_2\frac{y^2T^2}{a^2} + \cdots + c_n\frac{y^nT^n}{a^n} + \cdots \\ &+ c_{-1}\frac{a}{yT} + c_{-2}\frac{a^2}{y^2T^2} + \cdots + c_{-n}\frac{a^n}{y^nT^n} + \cdots \end{aligned}$$

Substituting this expansion into the integral in (9) yields

$$\begin{aligned} \int_0^\infty F(\lambda)\mathrm{e}^{-a/(\lambda T)}\mathrm{d}\lambda &= \frac{a}{T}\int_0^\infty F(\frac{a}{yT})\mathrm{e}^{-y}\frac{\mathrm{d}y}{y^2} \\ &= \sum_n c_n\frac{T^{n-1}}{a^{n-1}}\int_0^\infty \mathrm{e}^{-y}y^{n-2}\mathrm{d}y \\ &= \sum_n c_n\frac{T^{n-1}}{a^{n-1}}\Gamma(n-1) \end{aligned}$$

Since this is proportional to T^4, coefficients c_j for $j \geq 5$ must identically be zero, which yields $F(\lambda) = \frac{C}{\lambda^5}$ where C is a constant.

Therefore, the energy density along the lines of the foregoing derivation has a form

$$\rho(\lambda, T) = \frac{C}{\lambda^5}\mathrm{e}^{-a/(\lambda T)}.$$

Choose $C = 2hc^2$ and $a = hc/\kappa$ where h is the Planck constant, c is the speed of light, and κ is the Boltzmann constant.

This distribution has a finite peak at a wavelength of
$\lambda_{max} = \frac{hc}{5\kappa T} \approx 0.2878 \frac{cm \cdot K}{T}$, however the distribution as a whole still fails to accurately describe low-frequency radiation emission
and does not provide a physical mechanism motivating its validity.

The previous use of Planck's constant retrospective and is merely arbitrary for fitting the relation to the empirical data.

To address the high frequency contributions to the ultraviolet catastrophe in the case of the Rayleigh-Jeans law,
Planck hypothesized that the energy of an oscillator of natural frequency v is restricted to integral multiples of a basic unit hv,
i.e., $E = nhv$ where n is any integer from 0 to ∞.

The discrete quantization implied by this hypothesis at first seems unphysical, since observations of macroscopic oscillators such as radio waves, pendulums, and springs suggest that the allowed values of energy are effectively continuous.

Part of the subtlety of Planck's hypothesis is that Planck's constant has a value of approximately $6.626 \times 10^{-34} J \cdot s$, thus, in short,
any explanations of phenomena which his hypothesis purports would be consistent in the limit with classical mechanics which is correct in the region of such observations.

A sketch of a derivation of Planck's distribution of energy now follows.

This derivation is motivated by the objectives of determining the probability that an oscillator has an energy corresponding to its n^{th} allowed value,
and that when n is very large, the discrete character of the energy is unimportant and is consistent in the limit with classical mechanics.

To enforce the agreement with classical results in the limit, choose the same function of the energy as in the classical theory, i.e., $\mathrm{e}^{-E/(\kappa T)}$.

The probability for a given energy $E_n = nhv$ is then

$$W(n)\ \mathrm{e}^{-E_n/(\kappa T)} = \mathrm{e}^{-nhv/(\kappa T)}$$

Next, use a formula for the geometric series $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$ to write a normalization of the previous expression as

$$W(n) = \frac{\mathrm{e}^{-nhv/(\kappa T)}}{\sum_{n=0}^{\infty} \mathrm{e}^{-nhv/(\kappa T)}(1-\mathrm{e}^{-hv/(\kappa T)})}$$

Thus the mean energy is

$$\begin{aligned}\bar{E} &= \sum_{n=0}^{\infty} E_n W(n) = (1-\mathrm{e}^{-hv/(\kappa T)}) \sum_{n=0}^{\infty} \mathrm{e}^{-nhv/(\kappa T)} nhv \\ &= hv(1-\mathrm{e}^{-hv/(\kappa T)}) \sum_{n=0}^{\infty} n\mathrm{e}^{-nhv/(\kappa T)}\end{aligned}$$

Next, use the following relation to evaluate the above sum

$$\sum_{n=0}^{\infty} n\mathrm{e}^{-n\alpha} = -\frac{\mathrm{d}}{\mathrm{d}\alpha} \sum_{0}^{\infty} \mathrm{e}^{-n\alpha} = -\frac{\mathrm{d}}{\mathrm{d}\alpha} \frac{1}{1-\mathrm{e}^{-\alpha}} = \frac{\mathrm{e}^{-\alpha}}{(1-\mathrm{e}^{-\alpha})^2}$$

Thus, the mean energy relation is

$$\bar{E} = \frac{hv\mathrm{e}^{-hv/(\kappa T)}}{1-\mathrm{e}^{-hv/(\kappa T)}}$$

Next, multiplying by δN yields the Planck distribution

$$U(v) = \frac{8\pi V}{c^3} hv^3 \frac{\mathrm{e}^{-hv/(\kappa T)}}{1-\mathrm{e}^{-hv/(\kappa T)}}$$

The exponentials in the Planck distribution can be expanded for small values of $hv/\kappa T$, and the first terms, which dominate the outcome of the sum, yield $\bar{E} = \kappa T$.

This is congruent with the classical result and is in agreement with the correctness of the Rayleigh-Jeans law for small values of $hv/\kappa T$.

For large $hv/\kappa T$, $\bar{E} \to hv\mathrm{e}^{hv/(\kappa T)}$, which leads to Wien's approximation.

Between these small and large limits such as in the visible spectrum of wavelengths, Planck's distribution is in excellent agreement with experiment at all temperatures.

The interpretation of Planck's hypothesis further asserts that the decrease in mean energy of the high-freqeuncy oscillators arises because bringing them to an excited state, which is rare, requires a great amount of energy.

Lowering v or raising T makes it more likely that the oscillator will gain a quanta of energy.

If the oscillator is excited to a high quantum number n, its behavior will be essentially classical because the basic unit of energy hv is considerably less than the mean available energy κT.

Recall that the initial classical derivation relied on the fact that the black-body spectrum is independent of the materials of which the walls are composed.

Planck did not begin from this notion, rather, he assumed that the cavity radiation was in equilibrium with material oscillators in the walls of the container, and that these material oscillators could give up or absorb radiant energy only in quanta according to $E = nhv$.

This step is almost imperative to explain the black-body material independence of the cavity radiation.

If any radiation were present in energies other than quanta of $E = hv$, it could not, by hypothesis, interact with matter and therefore would not be detectable.

Conversely, it must be the case that *all* matter, and not only harmonic oscillators, can absorb or emit radiation in integer quanta of energy hv.

Planck's hypothesis is thus equivalent to the statement that all radiation oscillators have their energies restricted to $E = nhv$.

The scope of Planck's starting assumption, that the material oscillators in the walls of the black-body could give up or absorb radiant energy only in quanta according to $E = nhv$, can be further assessed by considering the specific heats of solids.

Specific heat capacity of a substance is the amount of heat that must be added to one unit of mass of the substance in order to cause an increase in one unit of temperature.

Before the advent of Planck's hypothesis,
French physicists Pierre Louis Dulong and Alexis Thérèse Petit proposed a thermodynamic law stating that
the heat capacity of a mole of many elementary solids with relatively simple crystal structure at temperatures far from absolute zero is about $3R$,
where R is the universal gas constant.

This is explained in terms of lattice vibrations in the solid.

Each atom in a crystal, for example, is in equilibrium when it is in its proper lattice position, and disturbances result in the atom oscillating about the equilibrium position with approximately simple harmonic motion for small oscillations.

Each atom can thus be approximated as an independent one-dimensional harmonic oscillator with one frequency v and possessing energy κT, which therefore contributes κ to the specific heat per atom.

Note that the proportionality factor $3R$ from the ideal gas constant and κ are physically the same but scaled for different sample sizes.

R is for one mole of substance, while κ is for one individual particle.

Specifically, 3 times the ideal gas constant R is approximately $24.942\ \mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}$ and the Boltzmann constant is $1.38 \times 10^{-23}\ \mathrm{J} \cdot \mathrm{K}^{-1}$.

Experimental evidence, however, shows that the specific heat approaches zero at absolute zero before rising asymptotically to the specific heat capacity ascribed by the Dulong-Petit law.

This demonstrates a failure of the classical Dulong-Petit law and a shortcoming of the equipartition theorem at cryogenic temperatures.

Einstein would proceed to apply Planck's hypothesis to this problem in his paper published in November of 1906, *"Planck's theory of radiation and the theory of specific heat"*.

Einstein's proposal in this paper was that specific heat capacity in this cryogenic region could be explained by assuming that the molecular oscillators are quantized according to Planck's relation $E = nhv$.

Thus, the material oscillators have only one frequency, the characteristic frequency of the substance, as opposed to the radiation oscillators which can have all possible frequencies.

Consider a solid of N atoms, which is equivalent to $3N$ independent, identical one-dimensional quantum harmonic oscillators.

Then, the mean energy per atom is $\bar{E} = \frac{hv}{\mathrm{e}^{hv/(\kappa T)-1}}$, so the specific heat per oscillator is given by

$$C_V = \frac{\mathrm{d}\bar{E}}{\mathrm{d}T} = \frac{\mathrm{d}}{\mathrm{d}T}\left(\bar{E} = \frac{hv}{\mathrm{e}^{hv/(\kappa T)-1}}\right)$$

Since

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\mathrm{e}^{hv/(\kappa T)}\right) = -\frac{hv}{\kappa T^2}\mathrm{e}^{hv/(\kappa T)}$$

$$\text{Thus } \Rightarrow C_V = \kappa\frac{(hv/(\kappa T))^2\mathrm{e}^{hv/(\kappa T)}}{(\mathrm{e}^{hv/(\kappa T)-1})^2}$$

Einstein's formula as $T \to \infty$ predicts that the specific heat per molecule $C_V \to \kappa$, and approaches zero at very low temperatures as

$$\frac{h^2v^2}{\kappa T^2}\mathrm{e}\frac{-hv}{\kappa T}$$

Einstein's theory is an improvement on the Dulong-Petit law as the first to apply quantization to explain why specific heat drops to zero as the temperature approaches absolute zero.

As such, it is a clear demonstration that Quantum Mechanics could solve the specific heat problem in classical mechanics.

Einstein's model of specific heat, in spite of its general agreement with experiment, was not completely accurate at very low temperatures on the order of 10° K.

This discrepancy would be rectified by Peter Debye's model, developed in 1912, by extimating the contribution of a quasi-particle known as a phonon.

The oscillations of each atom are actually not independent, but are coupled because of intermolecular forces.

Debye's model treats atmoic vibrations as collective quantized sound waves from the phonons within a continuous medium.

The Debye model accurately predicts that heat capacity vanished on the order of $\propto T^3$ at cryogenic temperatures and obeys the Dulong-Petit model at high temperatures.

Coupled oscillations can be described by considering a one-dimensional string of particles.

A similar treatment can be given in three dimensions to therefore describe the propagation of sound waves through a crystal.

Suppose that each particle interacts only with its two nearest neighbors.

Waves can then be shown to propagate through this system resembling waves propagating through a chain,
except that the waves are both longitudinal and transverse in this proxy-crystal system,
whereas the waves in a chain are only transverse.

For wavelengths that are large compared to the distance between particles, the wave propagation is marginally different from that in a continuous string, however, as the length of the waves approaches the mean distance between particles or smaller, propagation becomes impossible.

In such a one-dimensional string of particles, let the equilibrium distance between particles be denoted a.

Suppose the force on the n^{th} particle is given by

$$F_n = -m\omega_0^2 \left[(x_n - x_{n-1}) + (x_n - x_{n+1})\right] = m\ddot{x}_n,$$

where x_n is the deviation of the n^{th} particle from its equilibrium position.

A solution of the form $x_n = A_n \mathrm{e}^{i\omega t}$, and show that it can be chosen that $A_n = \mathrm{e}^{i\alpha n}$, where α is a suitable constant whose relationship to ω is obtained by the solution being sought.

From Newton's second law, $m\ddot{x}_n = F_n$,

$$\ddot{x}_n = -\omega_0^2 \left[(x_n - x_{n-1}) + (x_n - x_{n+1})\right] = -\omega_0^2(2x_n - x_{n-1} - x_{n+1}). \tag{10}$$

From $x_n = A_n \mathrm{e}^{i\omega t}$, then $\ddot{x}_n = -\omega^2 A_n \mathrm{e}^{i\omega t}$.

Substituting this into (10) and dividing by $\mathrm{e}^{i\omega t}$ yields

$$-\omega^2 A_n = -\omega_0^2(2A_n - A_{n-1} - A_{n+1}).$$

The choice of $A_n = \mathrm{e}^{i\alpha n}$ implies that $A_{n\pm1} = \mathrm{e}^{i\alpha(n\pm1)} = \mathrm{e}^{\pm i\alpha}\mathrm{e}^{i\alpha n}$, therefore

$$-\omega^2 \mathrm{e}^{i\alpha n} = -\omega_0^2(2\mathrm{e}^{i\alpha n} - \mathrm{e}^{-i\alpha}\mathrm{e}^{i\alpha n} - \mathrm{e}^{i\alpha}\mathrm{e}^{i\alpha n}) = -\omega_0^2 \mathrm{e}^{i\alpha n}(2 - \mathrm{e}^{-i\alpha} - \mathrm{e}^{i\alpha}).$$

Hence

$$\omega^2 = \omega_0^2(2 - \mathrm{e}^{i\alpha} - \mathrm{e}^{-i\alpha}) = \omega_0^2(2 - 2\cos\alpha) = 2\omega_0^2(1 - \cos\alpha).$$

Using the trigonometric identity $1 - \cos\alpha = 2\sin^2(\alpha/2)$,

$$\omega^2 = 4\omega_0^2 \sin^2(\frac{\alpha}{2}), \quad \omega = 2\omega_0 |\sin(\frac{\alpha}{2})|$$

Therefore, α is determined by ω up to sign and periodicity in α.

Next, show that for low frequencies the oscillations resemble sound waves, and that $\omega \approx 2\pi v/\lambda$ or equivalently $\omega \approx v_s k$ where $v_s = \omega_0 a$ is the speed of sound in the system.

In the low-frequency limit,
ω is small, therefore $|\sin(\alpha/2)|$ is small, therefore α is small,
therefore $\sin(\alpha/2) \approx \alpha/2$,

$$\text{therefore,} \quad \omega \approx 2\omega_0 \frac{|\alpha|}{2} = \omega_0|\alpha|.$$

Next, consider the wave number.

The spatial period of $A_n = \mathrm{e}^{i\alpha n}$ in the discrete index n corresponds to a spatial coordinate $x = na$, so the phase is $\alpha n = (\alpha/a)(na) = kx$ with $k = \alpha/a$.

Therefore, $\alpha = ka$, and

$$\omega \approx \omega_0|k|a = v_s|k|, \quad v_s = \omega_0 a.$$

Thus the dispersion of sound waves is given by $\omega \approx v_s k$ and $v_s = \omega_0 a$ is the speed of sound.

In terms of wavelength $\lambda = 2\pi/k$ and frequency $v = \omega/(2\pi)$,
$\omega \approx 2\pi v$ and $k = 2\pi/\lambda$, so $\omega \approx v_s \cdot 2\pi/\lambda$, i.e., $v \approx v_s/\lambda$.

Finally, show that there is a maximum possible frequency.

From $\omega = 2\omega_0|\sin(\alpha/2)|$, the maximum occurs when $|\sin(\alpha/2)| = 1$, i.e., $\alpha/2 = \pm\pi/2$, so $\alpha = \pm\pi$.

Therefore, $\omega_{max} = 2\omega_0$.

For $\alpha = \pi,\ A_n = \mathrm{e}^{i\pi n} = (-1)^n$, and so adjacent masses oscillate out of phase.

This is the shortest wavelength supported by the discrete lattice i.e., a wavelength of $\lambda = 2a$, and there is no propagation for $\omega > 2\omega_0$.

As was done with the electromagnetic field, the amplitudes of the possible sound waves can be adopted as coordinates to describe the state of the system.

Since these cordinates oscillate harmonically with time, the energy of the associated oscillators must be quantized.

Only a finite number of wavelengths is permissible, and the relation between frequency and wavelength becomes more complex as wavelengths comparable to interatomic spacing are approached.

These facts must be taken into account in computing the energy.

In all, these factors suggest that the quantum hypothesis leads to excellent general agreement with experimental specific heats at all temperatures.

Furthermore, in addition to the quantization of electromagnetic energy, there is evidence for the existence of the quantization of sound energy.

The conclusion is therefore that all systems which oscillate harmonically are quantized with $E = nhv$, whether these systems are material oscillators, sound waves, or electromagnetic waves.

The assumption that all systems can interact with each other implies that the quantization of any one type of harmonic oscillator requires a similar quantization of all other types.

Without this unity being experimentally evident, the quantum theory would need to be abandoned or at least fundamentally modified.