A Rigorous Thermodynamic Derivation of Planck's Radiation Law Without Postulating Kirchhoff's Law

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Abstract

We present a rigorous and modern thermodynamic derivation of Planck's radiation law. A key feature of this approach is the independent derivation of Kirchhoff's law of thermal emission (the condition $\varepsilon(\nu) = a(\nu)$) from the fundamental requirements of thermal equilibrium and the second law of thermodynamics, rather than postulating it. Subsequently, by combining this derived condition with the principles of statistical mechanics—specifically the entropy maximization of quantized electromagnetic modes within a cavity—we obtain the Planck distribution from first principles. This methodology provides a conceptually clearer and more unified foundation for blackbody radiation, firmly establishing its universal character as an inherent manifestation of equilibrium in quantized fields.

1 Introduction

The problem of blackbody radiation stands as a pivotal historical challenge that spurred the development of quantum theory. Central to its early understanding was Gustav Kirchhoff's law of thermal radiation, which posits a universal relationship between the emissivity $\varepsilon(\nu)$ and absorptivity $a(\nu)$ of any body in thermal equilibrium, specifically $\varepsilon(\nu) = a(\nu)$. While immensely useful, the traditional presentation of Kirchhoff's law often introduces this equality as a foundational postulate, thereby necessitating further justification or relying on idealized "black" surfaces.

In this paper, we aim to provide a more rigorous and self-contained derivation of Planck's radiation law, re-evaluating the role of Kirchhoff's law. Instead of assuming the emissivity-absorptivity relationship, we will derive it as a necessary consequence of the laws of thermodynamics applied to a system in equilibrium. This derived condition, coupled with the application of quantum statistical mechanics—specifically, the entropy maximization principle for a system of photons in a cavity—will allow us to deduce the Planck distribution entirely from fundamental principles.

This approach offers a conceptually cleaner and more robust foundation for understanding blackbody radiation, emphasizing its universal nature as a direct outcome of quantum mechanics and thermodynamics. The derivation proceeds through three main stages:

1. Establishing the universality of cavity radiation using thermodynamic arguments

2. Deriving Kirchhoff's law as a consequence of thermal equilibrium

3. Applying quantum statistical mechanics to obtain the explicit functional form

2 The Universality of Cavity Radiation and the Derivation of Kirchhoff's Law

Consider an evacuated cavity of arbitrary shape, with walls composed of any material, held at a uniform and constant temperature T. We assert that, under conditions of thermodynamic equilibrium, the spectral energy density of the radiation field within this cavity, $u(\nu, T)$, and consequently its spectral radiance $B(\nu, T)$, must be universal functions of frequency ν and temperature T, independent of the specific properties (material, shape, surface characteristics) of the cavity walls.

2.1 Proof of Universality by the Second Law of Thermodynamics

To demonstrate this universality, we employ a proof by contradiction based on the second law of thermodynamics. Consider two such cavities, Cavity A and Cavity B, constructed from different materials (e.g., copper and silver) but both maintained at the same temperature T. Let us assume, for the sake of contradiction, that their internal equilibrium radiation fields are different, i.e., $u_A(\nu, T) \neq u_B(\nu, T)$ for some frequency ν.

Now, consider connecting these two cavities via a narrow tube containing an ideal narrow-band filter. This filter allows only radiation within a small frequency range $[\nu, \nu + \Delta\nu]$ to pass through, reflecting all other frequencies.

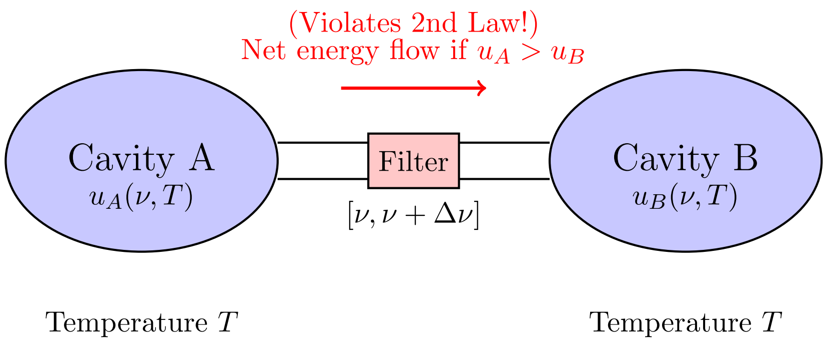

Figure 1: Thought experiment for proving the universality of cavity radiation. Two cavities at the same temperature are connected by a narrow-band filter. If the spectral energy densities differ, a net energy flow would occur, violating the second law of thermodynamics.

If $u_A(\nu, T) > u_B(\nu, T)$ for a given ν, then upon opening the filter, there would be a net flow of energy from Cavity A to Cavity B through the tube at that specific frequency. This energy transfer would occur spontaneously between two systems already at the same temperature, implying that one cavity would effectively "cool" while the other "heats up," or that work could be extracted from this spontaneous flow.

This scenario directly violates the second law of thermodynamics, which states that heat cannot spontaneously flow between bodies at the same temperature without external work, nor can work be continuously extracted from a single heat reservoir. The violation is particularly clear when we consider that such a device could be used to construct a perpetual motion machine of the second kind.

Therefore, our initial assumption must be false. For thermodynamic equilibrium to hold, the spectral energy density of the radiation field within any cavity at a given temperature T must be universal, independent of the wall properties:

$$u(\nu, T) = \text{universal function of } \nu \text{ and } T \tag{1}$$

Consequently, the spectral radiance $B(\nu, T)$ (the power emitted per unit area per unit solid angle per unit frequency into a hemisphere) must also be a universal function:

$$B(\nu, T) = \text{universal function of } \nu \text{ and } T \tag{2}$$

A small hole in the wall of such a cavity behaves as an ideal blackbody emitter because any radiation entering is absorbed and thermalized within the cavity, and any radiation escaping is precisely the universal equilibrium radiation. Thus, the universal function $B(\nu, T)$ is precisely the blackbody spectrum.

2.2 Derivation of Kirchhoff's Law

Now, let us consider an arbitrary body (or a small patch of the cavity wall itself) with spectral emissivity $\varepsilon(\nu)$ and spectral absorptivity $a(\nu)$, placed inside the universal radiation field of the cavity at temperature T. For this body to be in thermal equilibrium with the surrounding radiation, its rate of energy emission must precisely balance its rate of energy absorption at every frequency ν.

The power emitted by the body per unit area per unit frequency interval is given by $\varepsilon(\nu)B_s(\nu, T)$, where $B_s(\nu, T)$ is the spectral radiance that the surface would have if it were radiating in isolation at temperature T.

The power absorbed by the body per unit area per unit frequency interval from the cavity radiation field is $a(\nu)B(\nu, T)$, where $B(\nu, T)$ is the universal spectral radiance of the cavity.

For thermal equilibrium, the emitted power must equal the absorbed power:

$$\varepsilon(\nu)B_s(\nu, T) = a(\nu)B(\nu, T) \tag{3}$$

As established in the previous section, $B(\nu, T)$ is the universal blackbody spectral radiance. Furthermore, for the body itself to be in thermal equilibrium at temperature T, its intrinsic emissive power $B_s(\nu, T)$ must be consistent with the equilibrium state.

The key insight is that if $B_s(\nu, T)$ were different from the universal $B(\nu, T)$, we could construct another thermodynamic contradiction. Consider replacing a small section of the cavity wall with our material. If this material emitted radiation different from the universal cavity radiation, it would disturb the equilibrium, leading to energy flows that violate the second law.

Therefore, any body in thermal equilibrium at temperature T must emit radiation characterized by the universal blackbody spectrum: $B_s(\nu, T) = B(\nu, T)$.

Substituting this into Equation (3):

$$\varepsilon(\nu)B(\nu, T) = a(\nu)B(\nu, T) \tag{4}$$

Since $B(\nu, T) > 0$ for any finite temperature and frequency, we can divide both sides by $B(\nu, T)$, leading directly to:

$$\boxed{\varepsilon(\nu) = a(\nu)} \tag{5}$$

This fundamental relationship, known as Kirchhoff's law of thermal radiation, is thus derived here as a necessary consequence of the system being in thermodynamic equilibrium and the universality of cavity radiation, rather than being introduced as an independent postulate.

3 Statistical Mechanics of Cavity Modes and Entropy Maximization

Having established the nature of the equilibrium radiation, we now proceed to derive its explicit functional form, $B(\nu, T)$, using the principles of quantum statistical mechanics. The electromagnetic field within a cavity can be understood as a collection of independent harmonic oscillators, corresponding to the allowed modes (standing waves) of the field.

3.1 Quantization of Energy and Density of States

According to quantum theory, each electromagnetic mode of frequency ν can only possess discrete energy levels, analogous to a quantum harmonic oscillator:

$$E_n = nh\nu, \quad n = 0, 1, 2, \ldots \tag{6}$$

where h is Planck's constant. Note that we have chosen the zero-point energy reference such that the ground state has energy 0 rather than $\frac{1}{2}h\nu$. This choice does not affect the final result for the radiation law, as we are interested in energy differences.

For a large cavity of volume V, the number of allowed electromagnetic modes in the frequency interval $[\nu, \nu + \mathrm{d}\nu]$ is given by the density of states $g(\nu)\mathrm{d}\nu$. This is a standard result from electromagnetic wave theory in a cavity with conducting walls [1]:

$$g(\nu)\mathrm{d}\nu = \frac{8\pi\nu^2 V}{c^3}\mathrm{d}\nu \tag{7}$$

The derivation of this expression involves:

- Counting the number of allowed wave vectors $\mathbf{k}$ satisfying the boundary conditions
- The factor $\frac{4\pi\nu^2}{c^3}$ comes from the volume of a spherical shell in k-space
- The factor of 2 accounts for the two independent polarization states of electromagnetic waves

3.2 Average Energy per Mode via Bose-Einstein Statistics

Photons are bosons with zero rest mass and zero chemical potential (since photon number is not conserved—photons can be freely created and destroyed through emission and absorption processes). For a system of bosons in thermal equilibrium at temperature T, the average occupation number $\langle n(\nu) \rangle$ for a mode of energy $h\nu$ is given by the Bose-Einstein distribution:

$$\langle n(\nu) \rangle = \frac{1}{\exp(h\nu/k_\mathrm{B}T) - 1} \tag{8}$$

where k_B is Boltzmann's constant. The zero chemical potential condition ($\mu = 0$) is crucial and reflects the fact that photons can be created and annihilated freely, unlike massive particles where particle number conservation imposes constraints.

The average energy associated with a single mode of frequency ν is then the product of the average number of photons in that mode and the energy of a single photon:

$$\langle E(\nu) \rangle = \langle n(\nu) \rangle h\nu = \frac{h\nu}{\exp(h\nu/k_\mathrm{B}T) - 1} \tag{9}$$

3.3 Entropy Maximization Approach

As an alternative derivation that reinforces our result, we can derive the same expression using the principle of maximum entropy. For a system of indistinguishable bosons, the entropy is given by:

$$S = k_\mathrm{B} \sum_i \left[(1 + \langle n_i \rangle) \ln(1 + \langle n_i \rangle) - \langle n_i \rangle \ln\langle n_i \rangle\right] \tag{10}$$

To find the equilibrium distribution, we maximize this entropy subject to the constraint of fixed total internal energy $U = \sum_i \langle n_i \rangle E_i$ and the constraint that photon number is not conserved (hence $\mu = 0$).

Using the method of Lagrange multipliers with $\beta = 1/k_B T$ for the energy constraint, the condition for maximum entropy is:

$$\frac{\partial S}{\partial \langle n_i \rangle} - \beta \frac{\partial U}{\partial \langle n_i \rangle} = 0 \tag{11}$$

This yields:

$$k_B \ln \left(\frac{1 + \langle n_i \rangle}{\langle n_i \rangle} \right) = \beta E_i \tag{12}$$

Solving for $\langle n_i \rangle$:

$$\langle n_i \rangle = \frac{1}{\exp(\beta E_i) - 1} = \frac{1}{\exp(E_i/k_B T) - 1} \tag{13}$$

This confirms our Bose-Einstein result and shows that the average energy per mode is indeed given by Equation (9).

3.4 Derivation of Planck's Law

The spectral energy density $u(\nu, T)$ (energy per unit volume per unit frequency interval) is obtained by multiplying the average energy per mode by the density of states per unit volume:

$$u(\nu, T) = \frac{g(\nu)}{V} \langle E(\nu) \rangle \tag{14}$$

$$= \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{\exp(h\nu/k_B T) - 1} \tag{15}$$

$$= \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp(h\nu/k_B T) - 1} \tag{16}$$

The spectral radiance $B(\nu, T)$ (power radiated per unit area per unit solid angle per unit frequency) is related to the spectral energy density by:

$$B(\nu, T) = \frac{c}{4\pi} u(\nu, T) \tag{17}$$

This relationship can be derived by considering the flux of isotropic radiation through a surface. The factor $c/4\pi$ accounts for the fact that only a fraction of the isotropic radiation field contributes to the flux in any given direction.

Substituting Equation (16) into Equation (17):

$$B(\nu, T) = \frac{c}{4\pi} \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp(h\nu/k_B T) - 1} \tag{18}$$

$$= \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/k_B T) - 1} \tag{19}$$

Therefore, Planck's radiation law is:

$$\boxed{B(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/k_B T) - 1}} \tag{20}$$

4 Physical Interpretation and Limiting Cases

4.1 Classical Limit: Rayleigh-Jeans Law

In the low-frequency limit where $h\nu \ll k_B T$, we can expand the exponential:

$$\exp(h\nu/k_B T) \approx 1 + \frac{h\nu}{k_B T} \tag{21}$$

This gives:

$$B(\nu, T) \approx \frac{2h\nu^3}{c^2} \frac{1}{h\nu/k_B T} = \frac{2\nu^2 k_B T}{c^2} \tag{22}$$

This is the classical Rayleigh-Jeans law, which agrees with classical statistical mechanics but leads to the ultraviolet catastrophe when integrated over all frequencies.

4.2 High-Frequency Limit: Wien's Law

In the high-frequency limit where $h\nu \gg k_B T$, the exponential dominates:

$$B(\nu, T) \approx \frac{2h\nu^3}{c^2} \exp(-h\nu/k_B T) \tag{23}$$

This exponential cutoff prevents the ultraviolet catastrophe and was historically important in the development of quantum theory.

4.3 Stefan-Boltzmann Law

The total power radiated per unit area (integrated over all frequencies and solid angles) follows from integrating the Planck function:

$$j = \pi \int_0^\infty B(\nu, T) \mathrm{d}\nu = \sigma T^4 \tag{24}$$

where $\sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2}$ is the Stefan-Boltzmann constant.

5 Conclusion

We have presented a comprehensive and rigorous derivation of Planck's radiation law, building upon foundational principles of thermodynamics and quantum statistical mechanics. The key contributions of this approach are:

1. **Thermodynamic Foundation**: We explicitly demonstrated that Kirchhoff's law $\varepsilon(\nu) = a(\nu)$ is not an independent postulate but emerges as a necessary consequence of maintaining thermal equilibrium in a universal radiation field, as dictated by the second law of thermodynamics.

2. **Universality Proof**: The universality of cavity radiation was rigorously established through a thermodynamic argument that shows any deviation would violate the second law.

3. **Statistical Mechanics**: We applied the statistical mechanics of quantized electromagnetic modes, treating them as quantum harmonic oscillators and employing Bose-Einstein statistics with zero chemical potential for photons.

4. **Entropy Maximization**: We showed that the same result can be obtained through entropy maximization, providing additional theoretical foundation.

This approach provides a more unified and logically consistent framework for understanding blackbody radiation. It underscores that the universality of the Planck spectrum is not merely an empirical observation, nor dependent on auxiliary assumptions like a pre-existing Kirchhoff's law, but is instead an inherent outcome of applying fundamental principles of quantum mechanics and thermodynamics to a system in equilibrium.

The derivation solidifies Planck's law as a cornerstone of modern physics, reflecting the profound interplay between energy quantization, statistical equilibrium, and thermodynamic principles. This foundation has far-reaching implications, from understanding stellar radiation and the cosmic microwave background [2] to applications in modern quantum optics and thermal engineering.

The methodology presented here serves as a template for deriving other fundamental results in statistical mechanics and quantum field theory, emphasizing the power of combining thermodynamic reasoning with quantum statistical principles.

Acknowledgments

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References

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