Theories of Everything:
Thermodynamics
Statistical Physics
Quantum Mechanics

Gert van der Zwan

Thermodynamics of Light
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❖ Old Problems
❖ Photon Gas
❖ Carnot Cycle
❖ Efficiency
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Pursuing this idea I came to construct arbitrary expressions for the entropy which were more complicated than those of Wien ... but acceptable. Among those expressions my attention was caught by

$$\frac{\partial^2 s_\nu}{\partial e_\nu^2} = \frac{\alpha}{e_\nu(\beta + e_\nu)}$$

which comes closest to Wien's in simplicity and ... deserves to be further investigated.

Max Planck

... a piece of mathematical jugglery without any correspondence to anything real in nature

Max Planck

19th Century Problems

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- The status of the second law and the nature of entropy. Are there limits of validity? Maxwell's demon and Boltzmann's universe.
- The role of dissipation and the direction of time.
- Luminiferous aether (resolved?).
- Thermodynamics and spectrum of light (resolved?).

The resolutions of the last two problems led to completely new fields in physics with puzzles and paradoxes of their own: quantum mechanics and relativity. We'll get to some of those new problems in due course.

Properties of the Photon Gas

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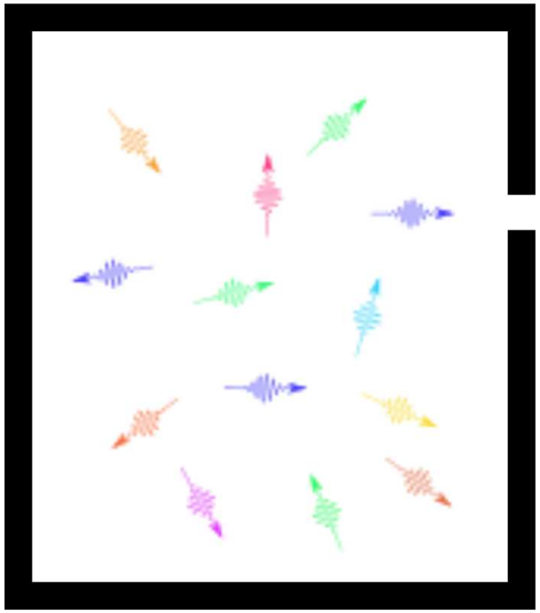

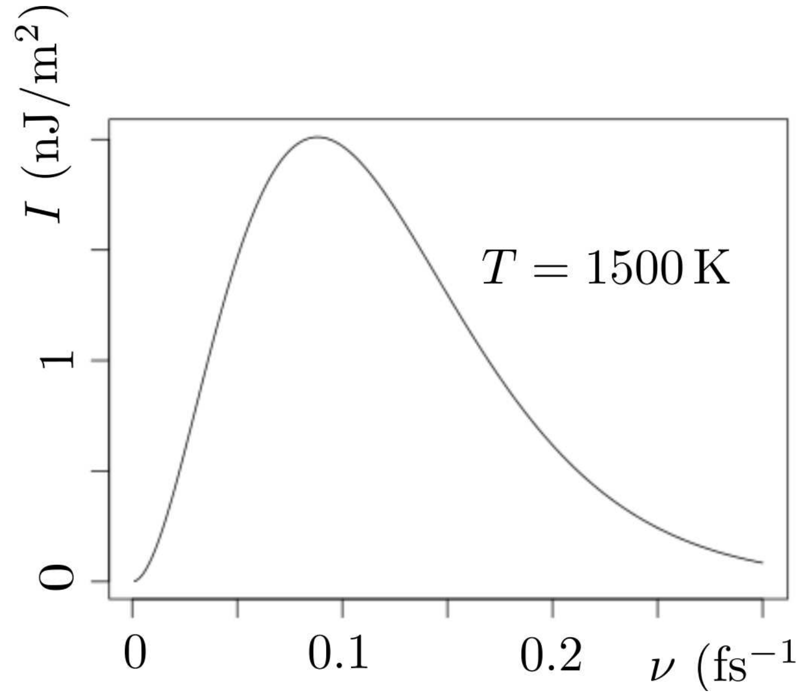

- $U = bVT^4$ en $p = \frac{U}{3V}$ (Wien, Boltzmann)
- $b = \frac{8\pi^5 k_B^4}{15c^3h^3} = 7.56577 \times 10^{-16}\,\mathrm{JK^{-4}m^{-3}}$

Isotherms and Adiabats

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- $p = \frac{U}{3V} = \frac{1}{3}bT^4$: isotherms are straight lines parallel to the V axis.
- Adiabats: $đq = 0$

$$
\begin{aligned}
dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = -pdV \\
&= 4bVT^3 dT + bT^4 dV
\end{aligned}
$$

so that

$$V dT = -\frac{1}{3} T dV$$

Integration gives

$$VT^3 = \text{constant} \quad \text{or} \quad pV^{4/3} = \text{constant}$$

Carnot Cycle for the Photon Gas

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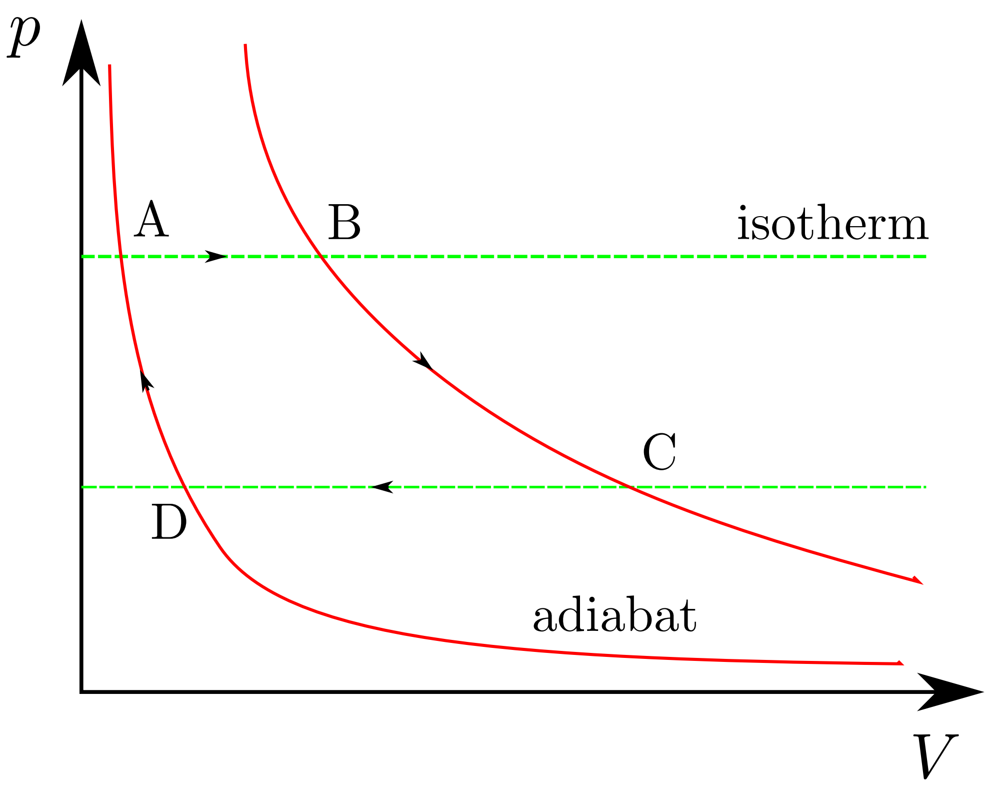

A→B: Reversible isothermal expansion:

$$w_{\mathrm{A}\to\mathrm{B}} = -\int_{\mathrm{A}}^{\mathrm{B}} p dV = -\frac{1}{3} b T_h^4 (V_B - V_A)$$

Carnot Cycle for the Photon Gas II

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- U is a state function:

$$\Delta U = bT_h^4(V_B - V_A)$$

- First law of thermodynamics:

$$q_{\mathrm{A}\to\mathrm{B}} = \Delta U - w_{\mathrm{A}\to\mathrm{B}} = \frac{2}{3}bT_h^4(V_B - V_A)$$

Exersize: calculate ΔU, q, and w for the other steps in the cycle.

- Efficiency:

$$\eta = 1 - \frac{q_{\mathrm{A}\to\mathrm{B}}}{q_{\mathrm{A}\to\mathrm{B}} + q_{\mathrm{C}\to\mathrm{D}}} = 1 - \frac{q_{\mathrm{A}\to\mathrm{B}}}{|q_{\mathrm{C}\to\mathrm{D}}|}$$

The Efficiency

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The efficiency is given by

$$\eta = \frac{\text{Work delivered}}{\text{Heat absorbed}} = \frac{-w_{\mathrm{A}\to\mathrm{B}} - w_{\mathrm{B}\to\mathrm{C}} + w_{\mathrm{C}\to\mathrm{D}} + w_{\mathrm{D}\to\mathrm{A}}}{q_{\mathrm{A}\to\mathrm{B}}} = 1 - \frac{T_l}{T_h} \quad (1)$$

Exactly the Carnot efficiency (as it should be).
Therefore

$$\eta = 1 + \frac{q_{\mathrm{A}\to\mathrm{B}}}{q_{\mathrm{C}\to\mathrm{D}}} = 1 - \frac{T_l}{T_h} \quad (2)$$

So that

$$\frac{q_{\mathrm{A}\to\mathrm{B}}}{T_h} + \frac{q_{\mathrm{C}\to\mathrm{D}}}{T_l} = 0 \quad (3)$$

Remember that the whole process is reversible.

Thermodynamic Entropy

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For all reversible cycles (not just Carnot):

$$\boxed{\oint \frac{dq}{T} = \oint dS = 0}$$

so that S is a state function.

How to calculate entropy changes:

1. Find a reversible path from the initial (i) to the final (f) state
2. Calculate
$$\Delta S = S_f - S_i = \int_i^f \frac{dq_{\mathrm{rev}}}{T} \tag{4}$$

The Second Law of Thermodynamics

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- Clausius: For all irreversible processes

$$\Delta S > \frac{q}{T}$$

- Corollary: For all processes in the universe

$$\boxed{\Delta S \geq 0}$$

Planck's road to the quantum

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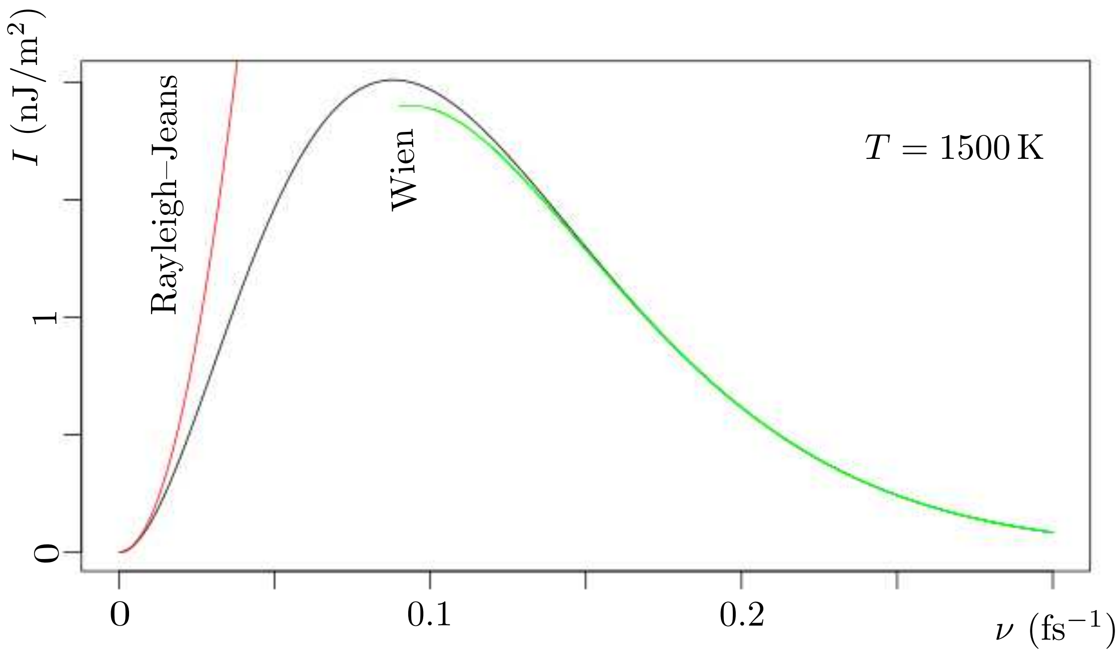

- Wien (using data fitting for high ν):

$$u_\nu = B\nu^3 e^{-\alpha\nu/T}$$

- Raleigh–Jeans (using the average oscillator energy):

$$u_\nu = \frac{2\pi\nu^2}{c^3}\langle E\rangle = \frac{2\pi\nu^2}{c^3}k_B T$$

Planck's road to the quantum II

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- Wien:
  - Correct in prediction of $\nu_{\mathrm{max}} \propto T$ (Wien's displacement law).
  - Correct in predicting $U \propto T^4$. (Stephan–Boltzmann).
  - Incorrect at low frequencies
- Rayleigh–Jeans:
  - Correct at low frequencies.
  - Ultraviolet catastrophy.
- Planck: Interpolate between the two behaviors (and find the constant B).

Planck's road to the quantum III

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1. Use thermodynamics

$$ds_\nu = \frac{1}{T}du_\nu + \frac{p}{T}dV \quad \Longrightarrow \quad \frac{1}{T} = \left(\frac{\partial s_\nu}{\partial u_\nu}\right)_V \tag{5}$$

2. Solve Wien and Rayleigh–Jeans for $1/T$:

$$\mathrm{W}: \quad \frac{1}{T} = \frac{k_B}{h\nu}\ln\frac{4B\nu^2}{cu_\nu}; \quad \mathrm{RJ}: \quad \frac{1}{T} = \frac{2\pi\nu^3 k_B}{c^3}\frac{1}{u_\nu} \tag{6}$$

3. Differentiate once more:

$$\mathrm{W}: \quad \frac{\partial^2 s_\nu}{\partial u_\nu^2} = -\frac{k_B}{h\nu}\frac{1}{u}; \qquad \mathrm{RJ}: \quad \frac{\partial^2 s_\mu}{\partial u_\nu^2} = -\frac{k_B}{h\nu}\frac{2\pi\nu^3 h}{c^3}\frac{1}{u^2} \tag{7}$$

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4. Interpolate:

$$\frac{\partial^2 s_\nu}{\partial u_\nu^2} = -\frac{k_B}{h\nu} \frac{1}{u_\nu + \frac{c^3}{2\pi\nu^2 h} u_\nu^2} \tag{8}$$

5. Integrate

$$\frac{1}{T} = -\frac{k_B}{h\nu} \int du_\nu \frac{1}{u_\nu + \frac{c^3}{8\pi\nu^2 h} u_\nu^2} = -\frac{k_B}{h\nu} \frac{\frac{c^3}{2\pi\nu^2 h} u_\nu}{1 + \frac{c^3}{8\pi\nu^2 h} u_\nu} \tag{9}$$

6. Invert:

$$\boxed{u_\nu = \frac{2\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1}} \tag{10}$$

The Temperature of Light

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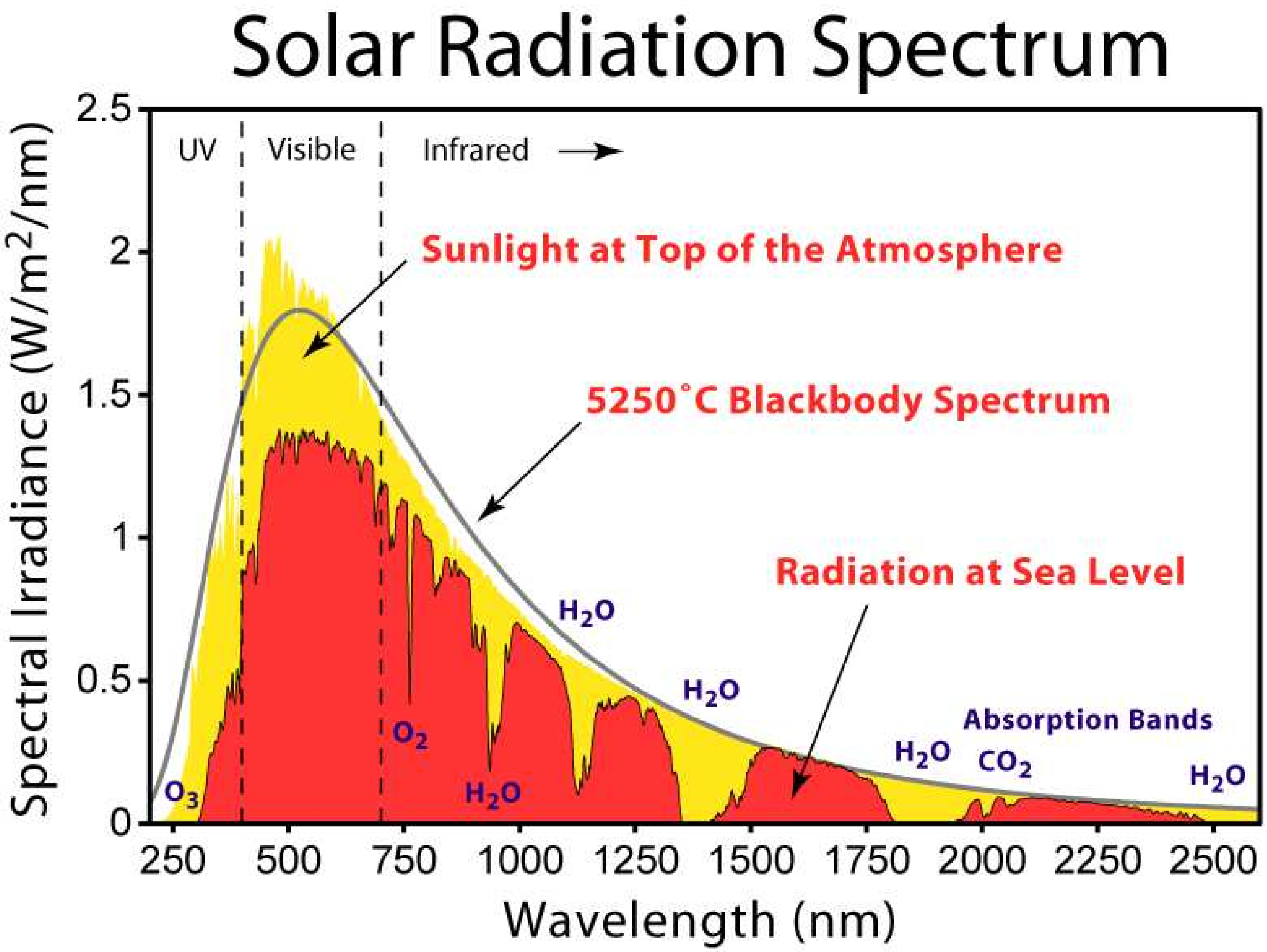

The Temperature of Light II

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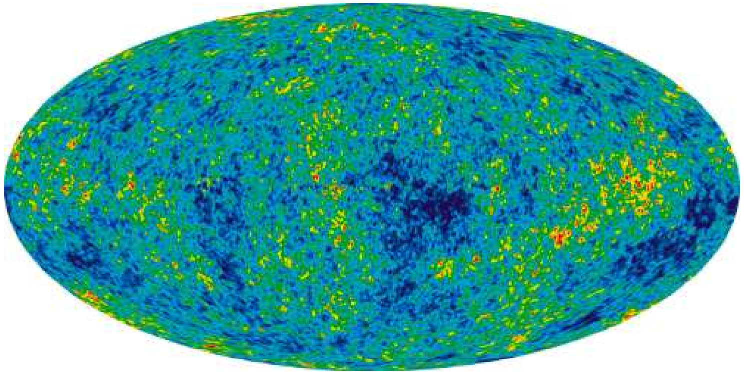

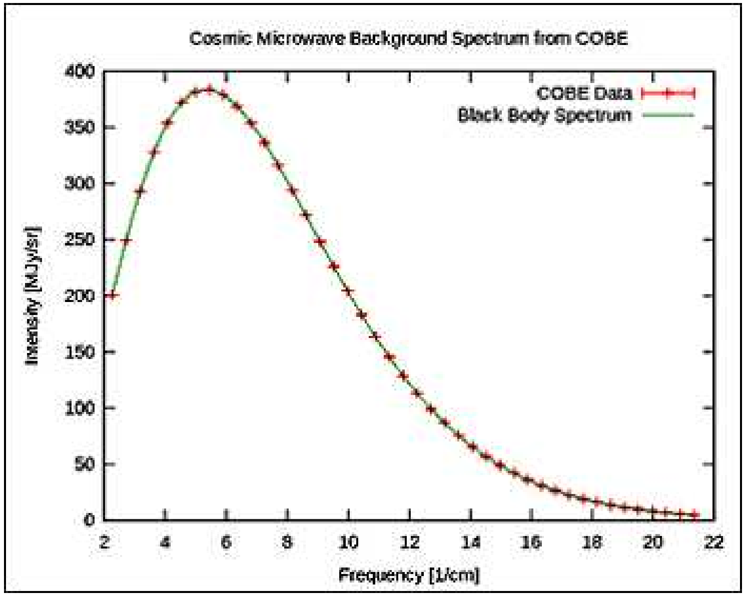

The temperature of the background radiation is 2.72548 ± 0.00057 K. There is no visible deviation from thermal equilibrium.

Mathematical Jugglery

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1. Average energy of the oscillator:

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/k_B T} - 1} \tag{11}$$

2. Elementary Statistical Mechanics

$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} \ln \frac{1}{1 - e^{-h\nu/k_B T}} = k_B T^2 \frac{\partial}{\partial T} \ln Q \tag{12}$$

3. Juggle:

$$Q = \frac{1}{1 - e^{-h\nu/k_B T}} = \sum_{n=0}^{\infty} e^{-nh\nu/k_B T} \tag{13}$$

The Upshot

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If Planck is correct, then the oscillator has (using Boltzmann's expression for the average energy of a system) discrete energies $nh\nu$, with $n = 0, 1, 2, \cdots$.

> My vain efforts to incorporate the quantum of action somehow into the classical theory took several years and much work. Some of my colleagues have seen this as tragic. But I disagree...
>
> Max Planck

> The only way to get revolutionary advances in science accepted is to wait for all old scientists to die.
>
> Max Planck, reflecting on himself.

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Equilibrium Canonical Partition Function

- Partition Function and Free Energy (Classical)

$$Q = \int d\Gamma\, e^{-\beta\mathcal{H}} \quad \text{and} \quad A = -k_B T \ln Q \tag{14}$$

- Partition Function and Free Energy (Quantum Mechanical)

$$Q = \mathrm{Tr}\left[e^{-\beta\mathcal{H}}\right] \quad \text{and} \quad A = -k_B T \ln Q \tag{15}$$

- Do exercises 8–11.

Decay of a Two–Level–System

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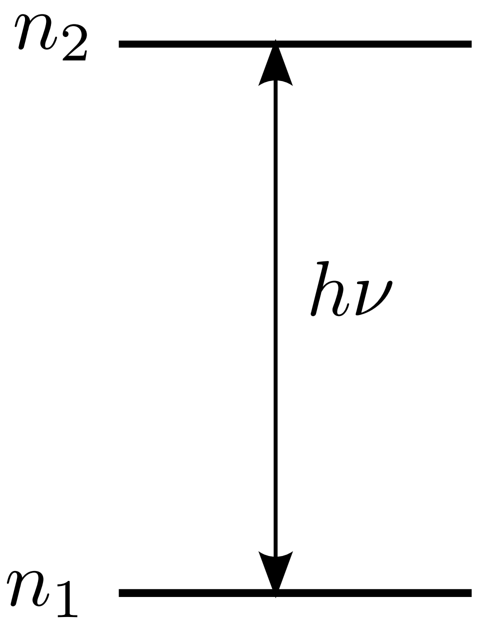

- n_1: number of 2LS's in the ground state; n_2: number of 2LS's in the excited state; N: total number of 2LS.
- Equilibrium distribution:

$$n_1 = \frac{N}{1 + e^{-\beta h\nu}} \tag{16}$$

- Dynamical Equations:

$$\frac{dn_1}{dt} = -BI(\nu)n_1 + An_2 \quad \text{and} \quad \frac{dn_2}{dt} = BI(\nu)n_1 - An_2 \tag{17}$$

Note that $N = n_1 + n_2$ does not depend on time.

Stationary Solution

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- Solution:

$$BI(\nu)n_1 - An_2 = 0 \quad \text{or} \quad \frac{n_1}{n_1 + n_2} = \frac{n_1}{N} = \frac{A}{A + BI(\nu)} \tag{18}$$

- Relation between A and B:

$$A = BI(\nu) + \frac{8\pi h\nu^3 B}{c^3} \tag{19}$$

- First term is called *Stimulated Emission* .
- Second term is *Spontaneous Emission*
- B depends on molecular properties, in particular the transition dipole moment.

Exercises and Problems

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1. Perform the calculations of ΔU, q, and w for the three other steps in the Carnot cycle of the photon gas.
2. Prove Eq. (1): the efficiency is equal to $\eta = 1 - \frac{T_l}{T_h}$.
3. Explore the differences between a photon gas and a classical ideal gas, also in relation to the respective Carnot cycles.
4. What is the contribution of the black body radiation energy to the total energy of a box of atoms at standard temperature and pressure?
5. Calculate the amount of heat needed for isothermal expansion of 1 m^3 of a photon gas to double its volume at 300 K. How is it possible that this is so much smaller than for a particle gas, while the efficiency of a Carnot engine based on either is the same?
6. If for all processes in the universe $\Delta S \geq 0$ and the background radiation coming from 350000 years after the big bang shows that the universe was in thermal equilibrium, how is it possible that anything interesting can have happened?
7. Show that $\Delta S \geq 0$ does not mean that for any subsystem of the universe the entropy cannot decrease.

Exercises and Problems 2

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8. The Hamiltonian for the classical Harmonic oscillator is $\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$. The phase space volume element is $d\Gamma = \frac{dp\,dx}{2\pi h}$. Calculate Q and A.
9. The Hamiltonian for the two–level system is $\mathcal{H} = \epsilon \left|1\right\rangle \left\langle 1\right|$. Calculate Q and A.
10. From thermodynamical relations, calculate the internal energy and the entropy for both the above cases.
11. The Hamiltonian for the quantum oscillator can be written as $\mathcal{H} = \hbar\omega \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \left|n\right\rangle \left\langle n\right|$. Calculate Q. Take the limit $T \to \infty$ and show that Q reduces to the result of exercise 8.
12. Derive Eq. (19).
13. Show that, if there is an additional mechanism of decay, such as energy transfer, or non–radiative decay, the population of the 2LS is that of a system at a lower temperature. Calculate that temperature as a function of the decay constant.
14. The fluorescence lifetime of bacteriochlorophyll (BCHl) is about 40 ns. The lifetime of (BCHl) in a photosynthetic antenna is of the order of 10 ps. What is the effective temperature of the BCHl pool in the antenna?

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