1
Radiation

1.1
Introduction

For the study of solar energy conversion, one needs to know how the photon flux of radiation is distributed over different photon energies E. The calculation of the spectral distribution $n(E)$ is supported by two distinct pillars:

- $h(E)dE$, i.e., the number of photon modes with energy in the range $(E, E + dE)$, and
- $f(E)$, i.e., the occupation probability of a mode with energy E.

Although we could postulate the functions $h(E)$ and $f(E)$, we will derive them from first principles. This is covered in Sections 1.2 and 1.3. Then, in Section 1.4, we will use these results to derive the radiation spectrum $n(E)$. Finally, in Section 1.5, we will see how $n(E)$ yields the total photon flux

$$N = \int_0^\infty n(E)\, dE$$

as well as the associated energy flux

$$Q = \int_0^\infty n(E) E\, dE$$

Any reader who wishes to skip the calculations of $h(E)$ and $f(E)$ can proceed immediately to Section 1.4.

1.2
Photon Modes ♡

We consider three-dimensional position space (x_1, x_2, x_3) and the corresponding three-dimensional momentum space (p_1, p_2, p_3). Together they form the six-dimensional hyperspace $(x_1, x_2, x_3, p_1, p_2, p_3)$, called the phase space. The three position coordinates x_i of a photon can have any value, ranging from $-\infty$ to $+\infty$, as can the three momentum coordinates p_i.

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Because a photon is a spin 1 particle, it has an additional coordinate, called the spin s. In contrast with the other six coordinates, the spin coordinate can have only two discrete values: -1 and $+1$. Therefore, the complete phase space of the photon consists of two six-dimensional hyperspaces, one with $s = -1$ (spin down) and one with $s = 1$ (spin up) (see Fig. 1.1).

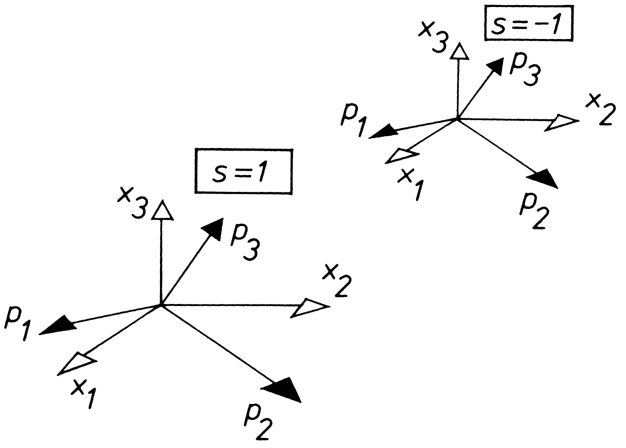

Fig. 1.1 Photon phase space.

Let dg be the number of modes with first position coordinate in the range $(x_1, x_1 + dx_1)$, with second position coordinate in the range $(x_2, x_2 + dx_2), \ldots,$ and third momentum coordinate in the range $(p_3, p_3 + dp_3)$. These modes occupy one of the two elemental hypervolumes

$$dx_1 \cdot dx_2 \cdot dx_3 \cdot dp_1 \cdot dp_2 \cdot dp_3 \tag{1.1}$$

After the Heisenberg principle of quantum mechanics one particle mode occupies a volume h^3. Here h is a fundamental constant of nature, i.e., Planck's constant 6.63×10^{-34} J s. Therefore dg equals the number of times h^3 fits into the two volumes (1.1):

$$dg = \frac{2\, dx_1 \cdot dx_2 \cdot dx_3 \cdot dp_1 \cdot dp_2 \cdot dp_3}{h^3} \tag{1.2}$$

Let g be the number of modes with momentum

$$\sqrt{p_1^2 + p_2^2 + p_3^2}$$

smaller than or equal to p. By simply integrating Eq. (1.2) with respect to the three space coordinates over the volume V and with respect to the three momentum coordinates over a sphere with radius p, we get

$$g = \frac{2V\frac{4}{3}\pi p^3}{h^3} \tag{1.3}$$

Here π is the mathematical constant, simply called pi, with the well-known numerical value 3.14159....

Because photons are particles with zero rest mass, they always travel at the same speed c, called the speed of light, i.e., 300 Mm/s, a second fundamental constant of nature. As a consequence, the energy E and the momentum p of the photon are related by the simple relativistic equation

$$E = cp$$

The number of photons with energy equal to or smaller than E is thus

$$g = \frac{\frac{8}{3}\pi V E^3}{c^3 h^3} \tag{1.4}$$

By differentiating with respect to E, we find the number of modes per unit of energy

$$\frac{dg}{dE} = \frac{8\pi V E^2}{c^3 h^3} \tag{1.5}$$

Having obtained the number of modes in the volume V, we now need the number of modes leaving this volume through a surface area S (see Fig. 1.2). Since radiation in a cavity is isotropic, i.e., uniformly distributed over all directions, a fraction $d\omega/4\pi$ has a propagation direction in the elemental solid angle $d\omega$. The photons with such a direction, hitting the surface area S in a time interval dt, occupy a cylindrical volume $V = Sc\cos\vartheta\, dt$, where ϑ is the

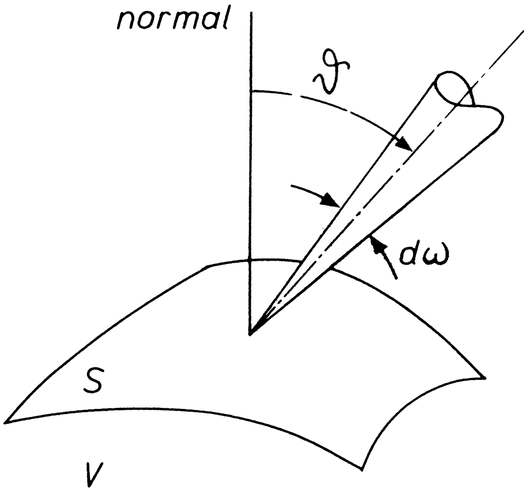

Fig. 1.2 Photon flux through a surface area S.

angle between the pencil $d\omega$ and the normal on S. Thus Eq. (1.5) becomes

$$\begin{aligned} \frac{dg}{dE} &= \frac{8\pi(Sc\cos\vartheta\,dt)(d\omega/4\pi)E^2}{c^3h^3} \\ &= \frac{2E^2}{c^2h^3}\,S\,dt\cos\vartheta\,d\omega \end{aligned} \tag{1.6}$$

Photons hit S from a hemisphere, i.e., from a solid angle 2π. Integration of Eq. (1.6) over this hemisphere yields

$$\frac{dg}{dE} = \frac{2\pi E^2}{c^2h^3}\,S\,dt$$

because of Lambert's geometrical law

$$\iint_{2\pi} \cos\vartheta\,d\omega = \pi \tag{1.7}$$

If we call $h(E)$ the number of photons hitting the boundary surface of the volume V per unit energy interval, per unit time, and per unit surface area, we eventually have

$$h(E) = \frac{2\pi}{c^2h^3}\,E^2 \tag{1.8}$$

The number of photons leaving the volume V along the other side of the surface is then given by

$$\epsilon(E)h(E) = \epsilon(E)\,\frac{2\pi}{c^2h^3}\,E^2$$

where ϵ is called the emissivity of the surface. The fraction $[1-\epsilon(E)]\,h(E)$ of the incident flux $h(E)$ is reflected by the surface S and thus sent back to the inside of the cavity volume V.

1.3
Photon Statistics ♡

As photons do not interact with each other, their statistical properties are entirely governed by their interaction with matter. Therefore, we necessarily need to know something more about the statistics of matter. Because we cannot reinvent all laws of physics from scratch, we will postulate some fundamental statistical laws of the solid state, without any proof.

The probability of a particular energy level with energy E to be occupied by an electron is

$$f(E) = \frac{1}{\exp\left(\frac{E-E_F}{kT}\right)+1} \tag{1.9}$$

where E_F is the Fermi energy and T the temperature associated with the matter reservoir, whereas k is a fundamental constant, i.e., the Boltzmann constant or 1.38×10^{-23} J/K. Up to now, we have introduced three fundamental constants of nature: h, c, and k. Figure 1.3 shows the function $f(E)$. We see that $f \approx 1$ for $E \ll E_F$, that $f = 1/2$ for $E = E_F$, and that $f \approx 0$ for $E \gg E_F$.

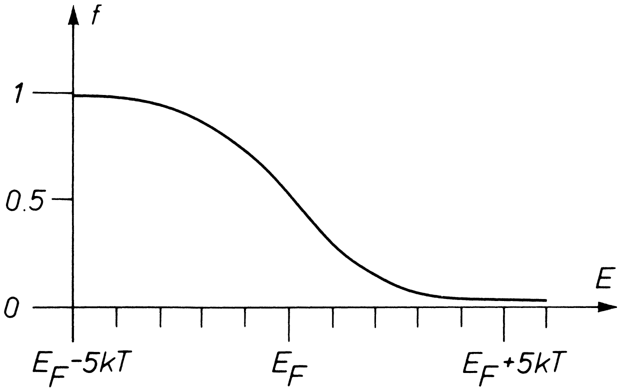

Fig. 1.3 The Fermi function.

Let us consider two states of matter, labeled 1 and 2, respectively. Let state 2 be the one with the higher energy

$$E_2 > E_1$$

We consider photons with energy E equal to the energy difference

$$E_2 - E_1$$

See Fig. 1.4. According to the Einstein model, these photons can interact with the matter in three different ways:

Stimulated absorption. An existing photon is absorbed by an electron at level 1, causing the electron to jump to level 2. The probability of the event is proportional to:

- f, i.e., the probability that there is a photon,
- f_1, i.e., the probability that level 1 is occupied, and
- $(1 - f_2)$, i.e., the probability that level 2 is not occupied.

Spontaneous emission. An electron falls spontaneously from level 2 to level 1 by emitting a photon. The probability of the event is proportional to

- f_2, i.e., the probability that level 2 is occupied, and
- $(1 - f_1)$, i.e., the probability that level 1 is not occupied.

Stimulated emission. Under influence of an already existing photon, an electron falls from level 2 to level 1 with emission of a second photon. The probability of the event is proportional to

- f, i.e., the probability that there already is a photon,
- f_2, i.e., the probability that level 2 is occupied, and
- $(1 - f_1)$, i.e., the probability that level 1 is not occupied.

This interaction model leads to the following kinetic equation:

$$\frac{df}{dt} = a[\,-ff_1(1-f_2) + f_2(1-f_1) + ff_2(1-f_1)\,]$$

In steady-state conditions $df/dt = 0$, so that

$$-ff_1(1-f_2) + f_2(1-f_1) + ff_2(1-f_1) = 0 \tag{1.10}$$

or

$$f = \frac{1}{\frac{f_1(1-f_2)}{(1-f_1)f_2} - 1} \tag{1.11}$$

After Eq. (1.9), we assume that

$$f_1 = \frac{1}{\exp\left(\frac{E_1-E_{F1}}{kT}\right)+1} \tag{1.12}$$

$$f_2 = \frac{1}{\exp\left(\frac{E_2-E_{F2}}{kT}\right)+1} \tag{1.13}$$

where we deliberately assumed that the two energy levels are at the same temperature T, but do not necessarily have the same Fermi energy E_F. By substitution of Eqs. (1.12) and (1.13) into Eq. (1.11), we immediately find

$$f = \frac{1}{\exp\left(\frac{E_2-E_1-E_{F2}+E_{F1}}{kT}\right)-1} \tag{1.14}$$

or

$$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{kT}\right)-1} \tag{1.15}$$

where

$$\mu = E_{F2} - E_{F1}$$

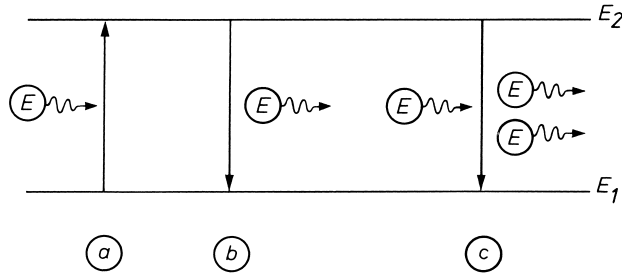

Fig. 1.4 Interaction of photons with two energy states of matter: (a) stimulated absorption, (b) spontaneous emission, (c) stimulated emission.

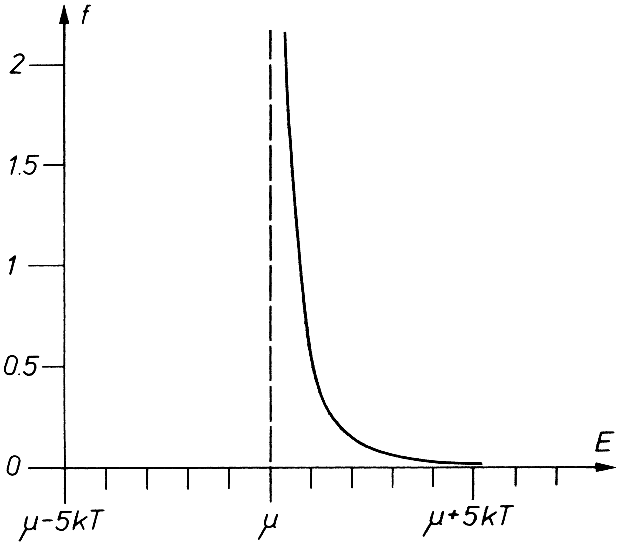

Fig. 1.5 The Bose function.

will be called the chemical potential of the photons. Equation (1.15) is called the Bose statistics of photons. Figure 1.5 shows the Bose function $f(E)$. We see that $f \to +\infty$ for $E \to \mu$ and $f \to 0$ for $E \to +\infty$. For $E < \mu$, Eq. (1.15) gives negative values, but makes no physical sense: for $E < \mu$, we actually have $f = 0$.

1.4
Planck's Law

The number of photons n in an energy range $(E, E + dE)$ is given by the product of the number of photon modes in the range and the occupation probability of these modes:

$$n(E) = \epsilon(E)h(E)f(E)$$

With the expression for $h(E)$ found in Section 1.2 and the expression for $f(E)$ found in Section 1.3, we get

$$n(E) = \epsilon(E)\,\frac{2\pi}{c^2h^3}\,\frac{E^2}{\exp\left(\frac{E-\mu}{kT}\right) - 1}$$

This important law is called Planck's law. Because a distribution over energies is often called a spectrum, we will call it Planck's spectrum.

The most well-known case is the radiation spectrum of a reservoir which has an emissivity ϵ independent of energy and which has a zero chemical potential μ:

$$\begin{aligned}\epsilon(E) &= \epsilon \\ \mu &= 0\end{aligned}$$

It is called the grey-body spectrum:

$$n(E) = \epsilon\,\frac{2\pi}{c^2h^3}\,\frac{E^2}{\exp\left(\frac{E}{kT}\right) - 1} \tag{1.16}$$

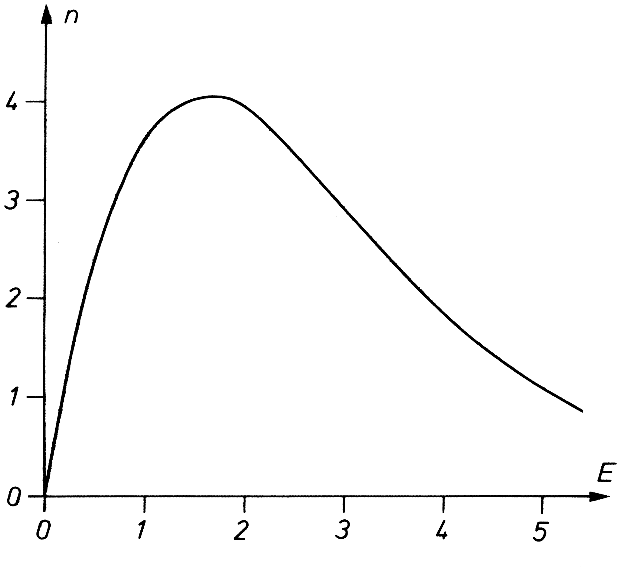

Fig. 1.6 The Planck spectrum with linear scales: E in units kT; n in units k^2T^2/c^2h^3.

The special case where ϵ equals unity is called the black-body spectrum. Figure 1.6 shows the black-body function $n(E)$. For small E, i.e., for $E \ll kT$, we have $\exp(E/kT) \approx 1 + (E/kT)$, so that $n(E)$ is proportional to E. For large E, i.e., for $E \gg kT$, $n(E)$ goes to zero like $E^2 \exp(-E/kT)$. For some intermediate value, called Wien's energy, the curve displays a maximum. Calculation of Wien's energy involves the numerical solution of a transcendental equation, yielding $E = 1.59362\ kT$. Thus the abscissa value of the maximum changes proportionally with temperature. This fact is called Wien's displacement law. The ordinate value of the maximum changes even more dramatically with temperature T. As a consequence we have to use logarithmic scales, if we want to plot different spectra for different temperatures on a single figure. An example is shown in Fig. 1.7. The three values chosen for T, i.e., 2.7, 288, and 5762 K, seem somewhat arbitrary. The reason for this choice will, however, become apparent in Chapter 2.

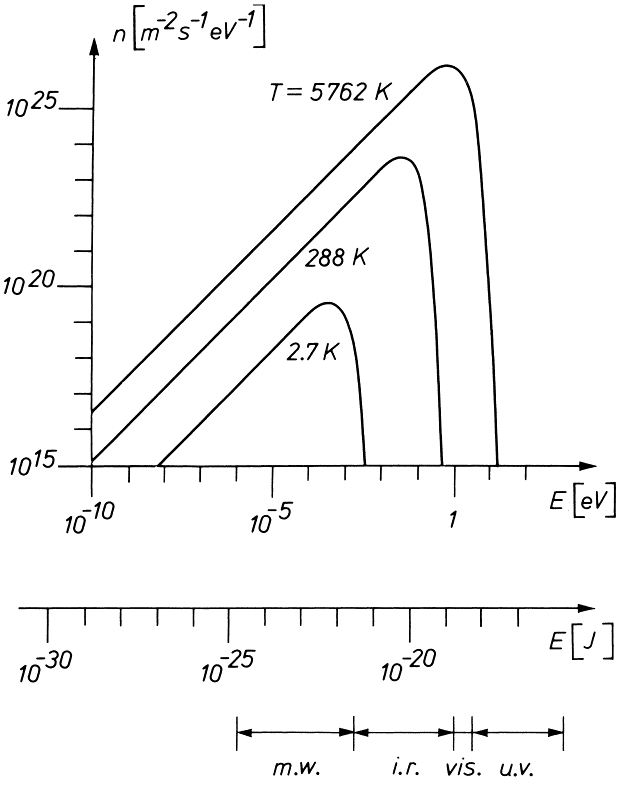

Fig. 1.7 The Planck spectrum with logarithmic scales (m.w., micro waves; i.r., infrared radiation; vis., visible light; u.v., ultraviolet radiation).

As we can see from Fig. 1.7, all three temperature examples give rise to spectra concentrated around energies, which are very small when expressed in the SI unit of energy, i.e., the joule. It is therefore advantageous to introduce a technical energy unit, i.e., the electronvolt. One electronvolt is defined as the energy of the elementary charge q at a voltage of 1 V. We have

$$1\ \mathrm{eV} = 1.60\ \times\ 10^{-19}\ \mathrm{J}$$

as q equals 1.60×10^{-19} C. Note that q is the fourth (and last) fundamental constant of nature that we introduce in the present book. The three other constants were: h, c, and k. See also Appendix A.

1.5
The Stefan–Boltzmann Law

By integrating the grey-body spectrum over all energies E, we obtain the total flux of photons (per unit time and per unit surface area):

$$\begin{aligned} N &= \int_0^\infty n(E)\,dE \\ &= \epsilon\,\frac{2\pi}{c^2h^3}\,(kT)^3 \int_0^\infty \frac{x^2dx}{\exp(x)-1} \end{aligned} \tag{1.17}$$

The definite integral at the end of this expression is written as $2\,\zeta(3)$ by mathematicians. Indeed, they define the Riemann zeta function $\zeta(n)$ by

$$(n-1)!\,\zeta(n) = \int_0^{+\infty} \frac{x^{n-1}dx}{\exp(x)-1}$$

The value of $\zeta(n)$ is tabulated and in the table we can find that $\zeta(3)$ equals about 1.20206. See Appendix A. Thus we finally find the number of photons emitted by a grey body:

$$N = 1.20206\,\epsilon\,\frac{4\pi k^3}{c^2h^3}\,T^3$$

We can also calculate the energy emitted by the body. For that purpose we have to calculate the integral

$$\begin{aligned} Q &= \int_0^\infty E\,n(E)\,dE \\ &= \epsilon\,\frac{2\pi}{c^2h^3}\,(kT)^4 \int_0^\infty \frac{x^3dx}{\exp(x)-1} \\ &= \epsilon\,\frac{2\pi}{c^2h^3}\,(kT)^4\,6\,\zeta(4) \end{aligned} \tag{1.18}$$

In contrast to $\zeta(3)$, the value of $\zeta(4)$ is not only to be found in the tables, it can also be reduced to a "simpler" mathematical number, i.e., π:

$$\zeta(4) = \frac{\pi^4}{90} = 1.08232$$

Therefore

$$Q = \epsilon \, \frac{2\pi^5 k^4}{15c^2h^3} \, T^4$$

This expression is so important that it has a name of its own: the Stefan–Boltzmann equation. The coefficient of T^4 has also a name: the Stefan–Boltzmann constant, with notation σ. The latter is not a fundamental constant of nature, as it can be expressed in terms of the three fundamental numbers h, c, and k:

$$\sigma = \frac{2\pi^5 k^4}{15c^2h^3}$$

Its value can thus be calculated and amounts to 5.67×10^{-8} W m^{-2} K^{-4}.

Thus we can write

$$Q = \epsilon \, \sigma T^4$$

Analogously, we can write

$$N = \epsilon \, \sigma' T^3$$

where σ' can also be expressed in terms of h, c, and k:

$$\sigma' = \frac{4\pi\zeta(3)k^3}{c^2h^3}$$

and has a value of 1.51×10^{15} s^{-1} m^{-2} K^{-3}. Oddly enough, σ' did not receive any name.

We end this section by noting that the average photon energy of grey (and of black) body radiation equals

$$\frac{Q}{N} = \frac{\sigma}{\sigma'} \, T = \frac{\pi^4}{30\zeta(3)} \, kT = 2.70117 \, kT$$

This number is somewhat larger than Wien's energy, 1.59362 kT. In the language of statistics we would say that the Planck distribution has a mean value larger than the mode.

1.6
Kirchhoff's Law

Until now, we have been concerned with the light emitted by a body. We also need to know something about the light absorbed by it. A black body absorbs all light incident on it. A nonblack body absorbs a fraction $\alpha(E)$ of the light incident on it, where α is called the absorptivity of the body. We now give, without proof, an important law of radiation physics, Kirchhoff's law, which states that the absorptivity exactly equals the emissivity:

$$\alpha(E) = \epsilon(E)$$

In particular, a grey body with emissivity ϵ will absorb exactly the fraction ϵ of all light incident on it.

1.7
Why T^4? ♡

As a result of the Stefan–Boltzmann law and the Kirchhoff law, two black surfaces facing each other exchange a net heat flux:

$$Q = \sigma S(T_1^4 - T_2^4)$$

where S is the surface area (assumed equal for the two surfaces) and where T_1 and T_2 are the temperatures of the bodies.

Why is radiation exchange governed by a fourth-power law? After all, heat conduction is satisfying a simpler equation:

$$Q = \frac{\lambda S}{d}(T_1 - T_2)$$

where λ is the heat conductivity of the medium between the two reservoirs and where d is the distance between the two surfaces (see Fig. 1.8). This law, sometimes called Fourier's law and sometimes called Newton's law, is linear like many so-called phenomenological or constitutive laws in physics. Ohm's law of electricity analogously states that the electrical current is proportional to the voltage difference $V_1 - V_2$. Fick's law of particle diffusion analogously states that the particle current is proportional to the concentration difference $n_1 - n_2$. Poiseuille's law says that the volume rate of a laminar fluid flow is proportional to the pressure difference $p_1 - p_2$.

So, why is the transport law of Stefan–Boltzmann not of this general type? Let us retrace the calculations of Sections 1.2–1.4 to find the answer. The T^4 proportionality appears in Eq. (1.18), where it is introduced by replacing $E^3 dE$ by $(kT)^4 x^3 dx$. Thus the T^4 is a consequence of the factor E^3 under the integral. This E^3 factor comes from $E\,n(E)$. Thus the T^4 is a consequence of $n(E)$ containing a factor E^2 in Eq. (1.16). This fact, in turn, is a consequence of $h(E)$ being proportional to E^2 in Eq. (1.8) and thus of g being proportional to E^3 in Eq. (1.4) or to p^3 in Eq. (1.3). So, we eventually retrieved the origin of the T^4 behavior of the Stefan–Boltzmann law: the volume of a sphere with radius p

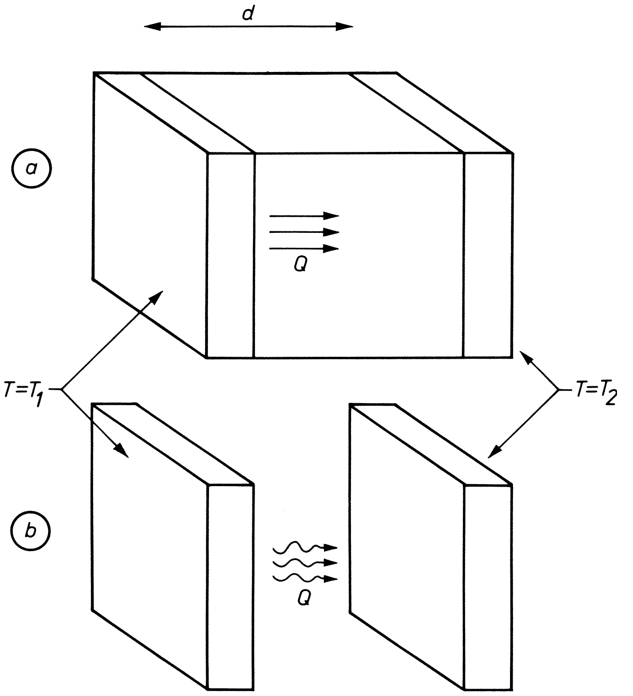

Fig. 1.8 Heat exchange by two surfaces: (a) by conduction, (b) by radiation.

equals $\frac{4}{3}\pi p^3$. The volume of a sphere being proportional to the third power of the radius is a consequence of space being three dimensional. Indeed, the volume of an n-dimensional hypersphere of radius p is proportional to p^n; it equals

$$V_n\, p^n$$

where V_n denotes a constant, independent of p. In fact V_n is the volume of the n-dimensional hypersphere with radius 1. Its value is dependent only on n. For $n = 3$, we have $V_3 = \frac{4}{3}\pi$. For other n, the value of V_n is tabulated in Appendix B.

If the universe were of n, rather than three dimensions, g would be proportional to E^n and $h(E)$ to E^{n-1}, and so $n(E)$ would contain a factor E^{n-1}. This would finally lead to a photon flux N proportional to T^n and a heat flux Q proportional to T^{n+1}. In other words, the power of T in the Stefan–Boltzmann law equals the number of space dimensions plus one. Explicit calculations [4] lead to the n-dimensional Stefan–Boltzmann law:

$$Q = \sigma_n T^{n+1}$$

where σ_n, i.e., the n-dimensional Stefan–Boltzmann constant, is given by

$$\sigma_n = r_n \, \pi^{(n-1)/2} \, \frac{\Gamma(n+1)\zeta(n+1)}{\Gamma\left(\frac{n+1}{2}\right)} \, \frac{k^{n+1}}{h^n c^{n-1}}$$

where $\Gamma(x)$ denotes the mathematical function called the gamma function and where r_n equals $n-1$, except for $n=1$ as $r_1 = 1$.

One can go one step further: why has our universe three spatial dimensions? The fact is: nobody in the world really knows. It is (still …) one of the great mysteries of nature. Did space always have three dimensions? Superstring theories suggest it did not. Shortly after its Big Bang birth, the universe could have had nine or even 25 spatial dimensions. In those early times, radiation was thus proportional to T^{10} or even T^{26}…

Analogous results can be formulated for the particle flux N. We have in n dimensions

$$N = \sigma_n' T^n$$

with

$$\sigma_n' = \frac{\zeta(n)}{n\zeta(n+1)} \, \frac{\sigma_n}{k}$$

We can only guess what the consequences of these facts would have been. Wisely, the remainder of this book will consider mostly three-dimensional space. We will make only about three excursions into hyperspace, just for fun.

1.8
Exercises

1.1 Check result (1.7):

$$\int_{\varphi=0}^{2\pi} \int_{\vartheta=0}^{\pi/2} \cos\vartheta \, (\sin\vartheta \, d\vartheta \, d\varphi) = \pi$$

1.2 Under which condition does stimulated emission exceed stimulated absorption?

1.3 Einstein's derivation of Eq. (1.14) was semiclassical and therefore not identical to the one presented above in Section 1.3. Einstein [1] started from

Boltzmann statistics of electrons:

$$f_1 = \frac{1}{\exp\left(\frac{E_1 - E_{F1}}{kT}\right)} \tag{1.19}$$

$$f_2 = \frac{1}{\exp\left(\frac{E_2 - E_{F2}}{kT}\right)} \tag{1.20}$$

instead of Eqs. (1.12) and (1.13). He did not take into account any Pauli exclusion principle and thus included neither a factor $(1 - f_2)$ into the absorption probability nor a factor $(1 - f_1)$ into the two emission probabilities, leading to steady state

$$-ff_1 + f_2 + ff_2 = 0$$

instead of (1.10). Demonstrate that this approach nevertheless gives rise to the same result (1.14).

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