Table 4.1 Several thermodynamic fluxes for photons with energies between ε_m and ε_M distributed according to a black body law determined by a temperature T and chemical potential μ. The last line involves the calculations for a full-energy spectrum ($\varepsilon_m = 0$ and $\varepsilon_M = \infty$). One of the results (the one containing T^4) constitutes the Stefan–Boltzman law

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$$\dot{\Omega}(T, \mu, \varepsilon_m, \varepsilon_M, H) = kT\frac{2H}{h^3\mathbf{c}^2}\int_{\varepsilon_m}^{\varepsilon_M} \ln(1 - \mathrm{e}^{(\mu-\varepsilon)/kT})\varepsilon^2\,\mathrm{d}\varepsilon = \int_{\varepsilon_m}^{\varepsilon_M} \dot{\omega}(T, \mu, \varepsilon, H)\,\mathrm{d}\varepsilon \qquad \text{(I-1)}$$

$$\dot{N}(T, \mu, \varepsilon_m, \varepsilon_M, H) = \frac{2H}{h^3\mathbf{c}^2}\int_{\varepsilon_m}^{\varepsilon_M} \frac{\varepsilon^2\,\mathrm{d}\varepsilon}{\mathrm{e}^{(\varepsilon-\mu)/kT}} - 1 = \int_{\varepsilon_m}^{\varepsilon_M} \dot{n}(T, \mu, \varepsilon, H)\,\mathrm{d}\varepsilon \qquad \text{(I-2)}$$

$$\dot{E}(T, \mu, \varepsilon_m, \varepsilon_M, H) = \frac{2H}{h^3\mathbf{c}^2}\int_{\varepsilon_m}^{\varepsilon_M} \frac{\varepsilon^3\,\mathrm{d}\varepsilon}{\mathrm{e}^{(\varepsilon-\mu)/kT}} - 1 = \int_{\varepsilon_m}^{\varepsilon_M} \dot{e}(T, \mu, \varepsilon, H)\,\mathrm{d}\varepsilon \qquad \text{(I-3)}$$

$$\dot{S} = \frac{\dot{E} - \mu\dot{N} - \dot{\Omega}}{T}; \quad \dot{F} \doteq \dot{E} - T\dot{S} = \mu\dot{N} + \dot{\Omega} \qquad \text{(I-4)}$$

$$\dot{E}(T, 0, 0, \infty, H) = (H/\pi)\sigma_{\mathrm{SB}}T^4; \dot{S}(T, 0, 0, \infty, H) = (4H/3\pi)\sigma_{\mathrm{SB}}T^3;$$

$$\sigma_{\mathrm{SB}} = 5.67 \times 10^{-8}\ \mathrm{Wm^{-2}\,K^{-4}} \qquad \text{(I-5)}$$

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a narrow cone of rays. In this case, $H = \pi A \sin^2\theta_s$, where θ_s is the sun's semi-angle of vision (taking into account the sun's radius and its distance to Earth), which is equal [13] to 0.267°. No index of refraction is used in this case because the photons come from the vacuum.

Fluxes of some thermodynamic variables and some formulas of interest, which can be obtained from the above principles, are collected in Table 4.1.

4.2.6 Thermodynamic Functions of Electrons

For electrons, the number of particles in a quantum state with energy ε is given by the Fermi–Dirac function $f_{\mathrm{FD}} = \{\exp[(\varepsilon - \varepsilon_F)/kT] + 1\}^{-1}$ where the electrochemical potential (the chemical potential including the potential energy due to electric fields) of the electrons is usually called *Fermi level*, ε_F. Unlike photons, electrons are in continuous interaction among themselves, so that finding different temperatures for electrons is rather difficult. In fact, once a monochromatic light pulse is shined on the semiconductor, the electrons or holes thermalise to an internal electron temperature in less than 100 fs. Cooling to the network temperature will take approximately 10 to 20 ps [14]. However, electrons in semiconductors are found in two bands separated by a large energy gap in which electron states cannot be found. The consequence of this is that, in non-equilibrium, different electrochemical potentials, ε_{Fc} and ε_{Fv} (also called *quasi-Fermi levels*), can exist for the electrons in the conduction band (CB) and the valence band (VB), respectively. Sometimes we prefer to refer to the electrochemical potential of the holes (empty states at the VB), which is then equal to $-\varepsilon_{Fv}$. Once the excitation is suppressed, it can even take milliseconds before the two quasi-Fermi levels become a single one, as it is in the case of silicon.