On the validity of Kirchhoff's law

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Abstract

Kirchhoff's law of heat radiation is a well-know law that can, under certain conditions, lead to a relationship of complimentarity between reflectivity ρ and emissivity ε ($\varepsilon = 1 - \rho$). However, the details of Kirchhoff's law and the situations in which it may be applied are not clearly understood, as evidenced by the debate in the literature. Here we outline the law and the main points of confusion regarding this law. We also give examples of situations in which Kirchhoff's law is not valid, such as paints with metallic particles, layered optical materials, or semi-infinite bodies with a large thermal gradient at the surface.

Introduction

In this document, we will discuss Kirchhoff's law of heat radiation, and the circumstances under which it is expected to hold, as well as those circumstances where the law is expected not to hold.

Kirchhoff's law of heat radiation states that the emissivity of radiating bodies in thermal equilibrium is equal to the absorptivity. More precisely, Baltes[1] summarizes Kirchhoff's law as follows:

> "For any body in (radiative) thermal equilibrium with its environment, the ratio between the spectral emissive power E(ν,T) and the spectral absorptivity *a*(ν,T) for a given frequency ν and temperature T is equal to the spectral emissive power E_{BB}(ν,T) of the blackbody for the same frequency and temperature."

Mathematically, it is given as follows:

Equation 1

$$E(\nu,T)/E_{BB}(\nu,T) = a(\nu,T)$$

The left-hand side of Equation 1 is nothing more than the spectral emissivity $\varepsilon(\nu,T)$, so we have

Equation 2

$$\varepsilon(\nu,T) = a(\nu,T)$$

In what follows, we will not include the frequency and temperature arguments; hence all quantities are assumed to be spectrally and thermally dependent, unless otherwise stated.

Kirchhoff listed several prerequisites needed for this law to hold, four of which the we list here for reference:

1. The radiation emitted by the body is independent from the environment.
2. The body radiates into empty space
3. The radiating body is inside a cavity with a non-transparent walls. These walls have the temperature of the radiating body.
4. The wavelengths occurring are infinitesimally small compared to all relevant length scales involved.

Confusion over Kirchhoff's law

Considerable confusion is found in the literature concerning Kirchhoff's law. Part of the confusion arises from the definition of the quantities used in Equation 2. The confusion stems from the definition of emission; namely whether induced (also called stimulated) emission should be included as positive emission or as negative absorption. Thus two definitions of emission are possible:

Equation 3

$$\varepsilon^{I} \equiv \varepsilon_{s} + \varepsilon_{i} = a_{i} \equiv a^{I}$$
$$\varepsilon^{II} \equiv \varepsilon_{s} = a_{i} - \varepsilon_{i} \equiv a^{II}$$

For the first definition of emissivity (ε^{I}), spontaneous (ε_s) and induced (ε_i) emission are both counted as emission. For the second definition of emissivity (ε^{II}), induced emission is considered negative absorption and is deducted from the absorptivity. We note that Kirchhoff's first prerequisite seems to favor ε^{II} because stimulated emission results from an interaction between the body in question and an external radiation field[1].

For a body in equilibrium, notably radiative equilibrium, both definitions hold. However, for a freely radiating body (i.e. a semi-infinite body radiating into free space) the distinction between the two definitions becomes more important because ε_i depends on the temperature of the environmental radiation field.

Of concern to engineers and experimentalists is the at what point the distinction between ε^{I} and ε^{II} becomes significant. Baltes shows that the distinction is not important as long as the following holds:

Equation 4

$$e^{(-hc/\lambda kT)} << 1$$

In Figure 1 we display the left-hand side of Equation 4 for several different temperatures.

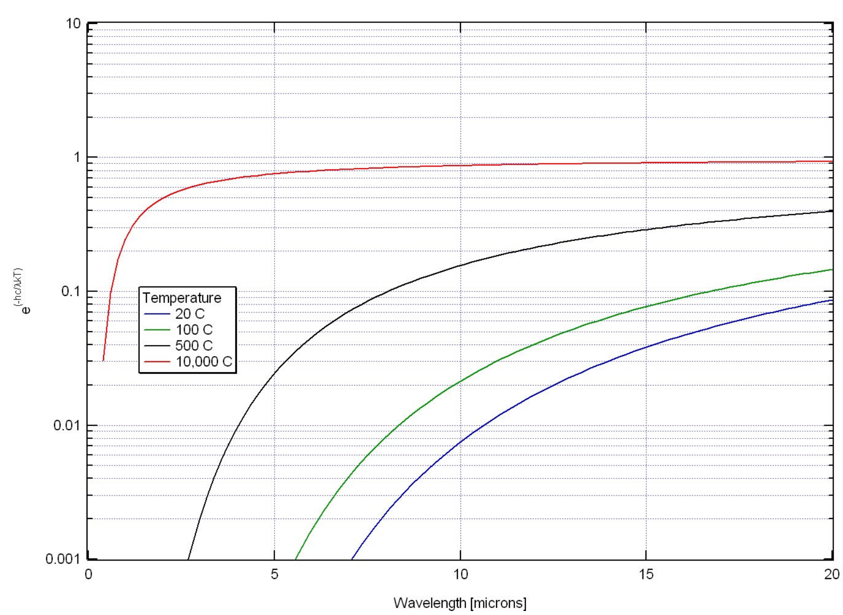

Figure 1: The exponential function of Equation 4 as a function of wavelength in microns, for several temperatures (see legend).

[1] In making this statement, we ignore second (and higher) order effects coming from induced emission due to interaction with photons generated by either spontaneous or induced emission.

Figure 4 shows that for band II (3 – 5 μm) and band III (8 – 12 μm), one can safely ignore the distinction between the two definition of emissivity given in Equation 3 for temperatures below 500 C (932 F).

Directional emissivity

Another point of confusion is the question of whether Kirchhoff's law holds for directional quantities or if it only holds for the total emissivity radiated in all directions into a hemisphere and the total absorptivity from all directions. The directional form of Kirchhoff's law can be written as follows:

Equation 5

$$\begin{aligned}\varepsilon_d(\theta,\phi) &= \alpha_d(\theta,\phi) \\ &= 1-\rho_d(\theta,\phi)\end{aligned}$$

where $\rho_d(\theta,\phi)$ is the directional reflectance, and, again, all quantities are all thermally and spectrally resolved.

This distinction comes into play if one intends to use Kirchhoff's law to derive the directional emissivity from the bidirectional reflectance distribution function (BRDF). Nicodemus[2] shows that Equation 5 holds due to the Helmhotz reciprocity law and Synder et al.[3] show that the Helmhotz reciprocity holds only for materials that are invariant under time reversal. Synder et al. give a simple example of a Faraday isolator (an optical device consisting of a Faraday rotator sandwiched between two linear, crossed polarizers) as a system that violates time reversal. They also give examples of materials that may potentially violate the directional for of Kirchhoff's law, among which they cite effects paints, such as paints with metal flakes, layered optical materials, and other materials in which multiple reflections and polarization effects are present.

Other cases for which Kirchhoff's law is observed to be violated include a freely radiating body with a large thermal gradient at the surface,[4,3] or systems whose energy states do not follow the Boltzman distribution.

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[1] H.P. Baltes, "On the validity of Kirchhoff's law of heat radiation for a body in a nonequilibrium environment", Progress in Optics XIII, ed. E. Wolf, North-Holland, 1976

[2] F. Nicodemus, "Directional Reflectance and Emissivity of an Opaque Surface", Applied Optics, vol. 4, p. 767, 1965.

[3] W.C.Synder, Z. Wan, and X. Li, "Thermodynamic constraints on reflectance reciprocity and Kirchhoff's law", Applied Optics, vol. 37, p. 3463, 1998.

[4] J.W. Salisbury, A. Wald, and D. M. D'Aria, "Thermal-infrared remote sensing and Kirchhoff's law", J. of Geophysical Research, vol. 99, no. B6, pp. 11,897 – 11,911, 1994.