

Non-equilibrium Stefan–Boltzmann law

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Abstract

We study thermal radiation outside equilibrium. The situation we consider consists of two bodies emitting photons at two different temperatures. We show that the system evolves to a stationary state characterized by an energy current which satisfies a law similar to the Stefan–Boltzmann law. The magnitude of this current depends on the temperature of the emitters expressed through the difference of the fourth power of these temperatures. The results obtained show how the classical laws governing the thermal radiation at equilibrium can be generalized away from equilibrium situations.

1 Introduction

Thermal radiation at equilibrium was studied by Planck [1] by using equilibrium thermodynamic concepts. The thermal properties of the gas of photons are well known. One of them, the Stefan–Boltzmann law [2], gives the value of the energy flux in terms of the temperature of the emitter through a power law σT^4 .

However, in many instances frequently found in nano-systems, the radiation is not in equilibrium due to the presence of thermal sources or temperature gradients. This is what happens in nanostructures such as solar cells and thermophotovoltaic devices [3, 4], even in cancer therapies [5, 6], just to cite some examples. In these situations, the classical scheme is no longer applicable and it then becomes necessary to employ a non-equilibrium theory. A first attempt to describe non-equilibrium radiation could be performed via non-equilibrium thermodynamics [8]. Nevertheless, some of the laws governing the behavior of thermal radiation are non-linear laws

whose derivation is beyond the scope of this theory, which provides only linear relationships between fluxes and forces.

In this article, we will show that this limitation can be overcome if mesoscopic non-equilibrium thermodynamics [9, 10] is used. This can be done by performing a description in terms of an internal variable [11, 12] – the momenta of the photons – and by assuming local equilibrium in phase space. In this way, it is possible to analyze the underlying activated process for which photons are emitted. The photon energy current obtained leads to the non-equilibrium Stefan–Boltzmann law.

This article is organized as follows: In Section 2, we study the photon gas outside equilibrium. Starting from the Gibbs entropy postulate, we derive the entropy production and from this the current of photons. In Section 3, we analyze the steady state obtained when photons are emitted by two bodies at two different temperatures. By using mesoscopic non-equilibrium thermodynamics, we derive the equivalent to the Stefan–Boltzmann law in this non-equilibrium situation. In the conclusion, we discuss some perspectives of the results obtained.

2 The non-equilibrium photon gas

Let us consider a gas of photons distributed through the law $n(\mathbf{\Gamma}, t)$ which is the probability density defined in the single-particle phase space $\mathbf{\Gamma} = (\mathbf{p}, \mathbf{x})$, where \mathbf{p} , \mathbf{x} are the momentum and position of a photon, respectively. According to the principle of the conservation of probability, we assume that $n(\mathbf{\Gamma}, t)$ satisfies the continuity equation

$$\frac{\partial}{\partial t} n(\mathbf{\Gamma}, t) = -\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \mathbf{J}(\mathbf{\Gamma}, t), \quad (1)$$

where $\partial/\partial \mathbf{\Gamma} = (\partial/\partial p, \nabla)$, $\nabla = \partial/\partial x$. The continuity equation (1) defines the probability current $\mathbf{J}(\mathbf{\Gamma}, t) = (J_x, J_p)$ which must be determined by means of the methods of non-equilibrium thermodynamics.

According to the Gibbs entropy postulate, our thermodynamic analysis of the non-equilibrium gas is based on the assumption of the density functional,

$$S(t) = -k_B \int n(\mathbf{\Gamma}, t) \ln \frac{n(\mathbf{\Gamma}, t)}{n_{\text{eq}}(\mathbf{\Gamma})} d\mathbf{\Gamma} + S_0, \quad (2)$$

as the non-equilibrium entropy of the system [8–10]. Here, S_0 is the equilibrium entropy of the gas plus the thermal bath and $n_{\text{eq}}(\mathbf{\Gamma})$ is the equilibrium probability density function.

By taking variations of Eq. (2), we obtain

$$\delta S = -k_B \int \delta n(\mathbf{\Gamma}, t) \ln \frac{n(\mathbf{\Gamma}, t)}{n_{\text{eq}}(\mathbf{\Gamma})} d\mathbf{\Gamma}, \quad (3)$$

where once one introduces the non-equilibrium chemical potential

$$\mu(\mathbf{\Gamma}, t) = k_B T \ln \frac{n(\mathbf{\Gamma}, t)}{n_{\text{eq}}(\mathbf{\Gamma})}, \quad (4)$$

Eq. (3) can be written as

$$\delta S = - \int \frac{\mu(\mathbf{\Gamma}, t)}{T} \delta n(\mathbf{\Gamma}, t) d\mathbf{\Gamma}. \quad (5)$$

Here, Eq. (5), which is the Gibbs equation of thermodynamics formulated in the phase space, illustrates the physical meaning of the non-equilibrium chemical potential (4). Since $-T\delta S = \delta F$, with F the non-equilibrium free energy, Eq. (5) leads to

$$\delta F = \int \mu(\mathbf{\Gamma}, t) \delta n(\mathbf{\Gamma}, t) d\mathbf{\Gamma}. \quad (6)$$

On the other hand, the equilibrium chemical potential of photons is zero, thus no reference value μ_0 is needed in Eq. (4). From Eqs. (1) and (5) we obtain the entropy production

$$\frac{\partial S}{\partial t} = - \int \mathbf{J}(\mathbf{\Gamma}, t) \cdot \frac{\partial}{\partial \mathbf{\Gamma}} \frac{\mu(\mathbf{\Gamma}, t)}{T} d\mathbf{\Gamma}, \quad (7)$$

as the product of a thermodynamic current and the conjugated thermodynamic force $\partial/\partial \mathbf{\Gamma}(\mu(\mathbf{\Gamma}, t)/T)$ [8]. As usual in non-equilibrium thermodynamics [8], from Eq. (7) we derive the phenomenological law

$$\mathbf{J}(\mathbf{\Gamma}, t) = -\mathbf{L}(\mathbf{\Gamma}) \cdot \frac{\partial}{\partial \mathbf{\Gamma}} \frac{\mu(\mathbf{\Gamma}, t)}{T}, \quad (8)$$

where $\mathbf{L}(\mathbf{\Gamma})$ is the matrix of phenomenological coefficients. Hence, Eq. (8) enables us to write the entropy production Eq. (7) as a bilinear form:

$$\frac{\partial S}{\partial t} = \int \frac{\partial}{\partial \mathbf{\Gamma}} \frac{\mu(\mathbf{\Gamma}, t)}{T} \cdot \mathbf{L}(\mathbf{\Gamma}) \cdot \frac{\partial}{\partial \mathbf{\Gamma}} \frac{\mu(\mathbf{\Gamma}, t)}{T} d\mathbf{\Gamma}. \quad (9)$$

In terms of the diffusion matrix $\mathbf{D}(\mathbf{\Gamma}) = k_B \mathbf{M}$, where $\mathbf{M}(\mathbf{\Gamma}) = \mathbf{L}/n$ is the mobility, Eq. (8) can be written in a more convenient form,

$$\mathbf{J}(\mathbf{\Gamma}, t) = -\mathbf{D}(\mathbf{\Gamma}) \cdot \frac{\partial}{\partial \mathbf{\Gamma}} n(\mathbf{\Gamma}, t), \quad (10)$$

which constitutes Fick's law of diffusion [13] formulated in the single-particle phase space.

3 Stationary state and the non-equilibrium Stefan–Boltzmann law

In this section we will study the heat exchange by thermal radiation between two bodies at different temperatures. This process comes into play in nanostructures such as solar cells and thermophotovoltaic devices, just to cite some examples. Applications of thermophotovoltaic devices range from hybrid electric vehicles to power sources for microelectronic systems [3]. Therefore, as mentioned, the recent developments of nanotechnology made the study of heat exchange by thermal radiation an object of growing interest [14].

Hence, to undertake this study, we assume that the dynamics of the photons is the result of two simultaneous processes: emission and absorption of cold photons at T_C and emission and absorption of hot photons at T_H ; this is illustrated by the Figure 1.

Since the photons do not interact among themselves we assume that the system is homogeneous, $\mathbf{\Gamma} \rightarrow \mathbf{p}$, and the diffusion matrix reduces to a scalar $D(\mathbf{\Gamma})$, the diffusion coefficient. Additionally, if there are only hot and cold photons

$$\mathbf{J}(\mathbf{p}, t) = \widehat{\mathbf{J}}_C(t)\delta(\mathbf{p} - \mathbf{p}_C) + \widehat{\mathbf{J}}_H(t)\delta(\mathbf{p} - \mathbf{p}_H), \quad (11)$$

i.e., the system reaches a state of quasi equilibrium. Thus, integration of Eq. (10) taking into account Eq. (11) leads to

$$\frac{\widehat{J}_C(t)}{D_C} + \frac{\widehat{J}_H(t)}{D_H} = -[n(\mathbf{p}_C, t) - n(\mathbf{p}_H, t)], \quad (12)$$

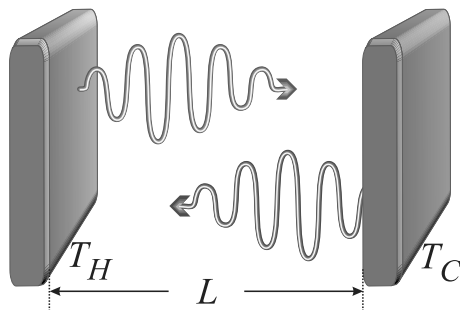


Figure 1. (Color online) Schematic illustration of the radiation exchanged between two materials maintained at different temperatures, T_H and T_C , separated by a distance L .

with $J(t) = \mathbf{u} \cdot \mathbf{J}(t)$ and \mathbf{u} being the unit vector normal to the walls. Whence, introducing the net current $J(t)$ defined through

$$\frac{J(t)}{aD_C D_H} = \frac{\widehat{J}_C(t)}{D_C} + \frac{\widehat{J}_H(t)}{D_H}, \quad (13)$$

or, equivalently,

$$J(t) = aD_H \widehat{J}_C(t) + aD_C \widehat{J}_H(t), \quad (14)$$

we can rewrite Eq. (12) as

$$J(t) = -aD_C D_H [n(\mathbf{p}_C, t) - n(\mathbf{p}_H, t)], \quad (15)$$

where a is an effective parameter accounting for the dimensionality. Here, term-by-term comparison of Eqs. (14) and (15) leads to the identification

$$\widehat{J}_C(t) = -aD_C n(\mathbf{p}_C, t), \quad (16)$$

$$\widehat{J}_H(t) = aD_H n(\mathbf{p}_H, t). \quad (17)$$

Therefore,

$$-D_H \widehat{J}_C(t) = D_H D_C n(\mathbf{p}_C, t) \quad (18)$$

represents the fraction of photons absorbed at the hot wall from the fraction $J_C(t)$ of photons emitted at the cold wall. In the same way,

$$D_C \widehat{J}_H(t) = D_C D_H n(\mathbf{p}_H, t) \quad (19)$$

represents the fraction of photons absorbed at the cold wall from the fraction $J_H(t)$ of photons emitted at the hot wall.

To better illustrate the physics under the non-equilibrium process involving the photons, we introduce the affinity

$$A = \mu_C - \mu_H, \quad (20)$$

where $\mu_C = \mu(\mathbf{p}_C, t)$ and $\mu_H = \mu(\mathbf{p}_H, t)$, which with the help of Eq. (4), enables us to rewrite Eq. (15) as [11]

$$J(t) = aD_C D_H \exp\left(\frac{\mu_H}{k_B T_H}\right) \times \left(1 - \exp\left(\frac{A}{k_B T_H}\right) \exp\left[\frac{\mu_H}{k_B} \left(\frac{1}{T_C} - \frac{1}{T_H}\right)\right]\right). \quad (21)$$

This result shows the non-linearity inherent to the process involving the radiation since this corresponds to a heat current that does not satisfy the Fourier law.

In general, the diffusion coefficient might depend on the frequency. However, one can introduce a cut-off limit, $\lambda_T = c\hbar/k_B T$, the thermal wavelength of a photon, which marks this dependence. So, for length scales $L \gg \lambda_T$ (i.e., high frequencies) we can treat the photons as point particles; hence in this case we deal with the free diffusion of point particles for which the diffusion coefficient is constant. On the other hand, when $L \lesssim \lambda_T$ (i.e., low frequencies) we deal with the problem of cage diffusion [15], therefore the diffusion coefficient must depend on the ratio λ_T/L or equivalently on the frequency [16, 17].

In the stationary state, the current of photons per unit of volume in phase space is given by

$$J_{st}(\omega) = a D_C(\omega) D_H(\omega) [n(\omega, T_H) - n(\omega, T_C)], \quad (22)$$

where

$$n(\omega, T) = 2 \frac{N(\omega, T)}{h^3}, \quad (23)$$

with h being the Planck constant and $N(\omega, T)$ the averaged number of particles in an elementary cell of the phase space given by the Planck distribution [2]:

$$N(\omega, T) = \frac{1}{\exp(\hbar\omega/kT) - 1}. \quad (24)$$

In Eq. (23) the factor 2 comes from the polarization of the photons. Here, the diffusion constant plays the role of the effective cross section.

By multiplying Eq. (22) by $\hbar\omega$ – the energy of a photon – and integrating in momentum space we obtain the heat current

$$Q = \int \hbar\omega J_{st}(\omega) d\mathbf{p}, \quad (25)$$

where $\mathbf{p} = (\hbar\omega/c)\mathbf{\Omega}_p$. In the case $L \gg \lambda_T$, and in an ideal situation, we can take $D_C = D_H = D = 1$. Thus, with Eq. (23), Eq. (25) leads to

$$Q = \frac{\hbar}{4\pi^3 c^3} \int d\omega d\mathbf{\Omega}_p \omega^3 J_{st}(\omega) = \sigma(T_H^4 - T_C^4), \quad (26)$$

where we have taken $a = c/4$, with c being the velocity of the radiation and

$$\sigma = \pi^2 k_B^4 / 60 \hbar^3 c^2$$

being the Stefan constant [2]. At equilibrium $T_H = T_C$, therefore $Q = 0$.

For an s -dimensional system, the phase space is made up of s coordinates and s conjugated momenta. Hence, the volume of an elementary cell of this phase space is h^s and now

$$n(\omega, T) = 2 \frac{N(\omega, T)}{h^s}. \quad (27)$$

In this case, by integrating over a hypersphere in momentum space and assuming that now a is a function of s , $a(s)$, it is possible to obtain

$$Q = \sigma(s)(T_H^{s+1} - T_C^{s+1}), \quad (28)$$

which generalizes results previously derived in Ref. [20].

4 Conclusions

In this paper we have performed a thermodynamic analysis of the radiative heat exchange between two bodies at different temperatures separated by a certain distance L . We have shown how the Stefan–Boltzmann law can be generalized to non-equilibrium situations such as those in which thermal radiation is composed by photons emitted at two different temperatures and thus having different momenta. In the framework of mesoscopic non-equilibrium thermodynamics based on the Gibbs entropy postulate, we have obtained the Gibbs equation of thermodynamics which here describes the local equilibrium in the phase space. Then, by means of the usual procedure of non-equilibrium thermodynamics, from the Gibbs equation we have derived Fick's law for the diffusion of photons valid at short time scales.

The exchange of energy is assumed to be due to activated processes related to reaction rate currents which are derivable in the framework of our thermodynamic theory. These currents provide us with the rate of absorption and emission of photons. Since in the stationary state both hot and cold photons are in local equilibrium, their rates are proportional to the Planck distribution. Finally, the net current of heat is given through a balance of these rate currents after integration over frequencies, constituting the non-equilibrium Stefan–Boltzmann law.

Systems outside equilibrium exhibit peculiar features not observed in an equilibrium state [7]. The results obtained show how non-equilibrium phenomena taking place in gases composed of quasi-particles, governed by non-linear laws, can be analyzed by means of the methods of non-equilibrium thermodynamics applied to the mesoscale. These methods have been shown to be very useful in the study of activated processes of different natures [18, 19].

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