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On the nonequilibrium generalization of the Wien displacement

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Abstract

The nonequilibrium extension of the Wien displacement is analyzed by taking into account the requirement of vanishing photon number flux. According to the vanishing-flux model, the nonequilibrium corrections to the Wien displacement are larger than previously thought [J. Fort, J.A. González and J.E. Llebot, Phys. Lett. A 236 (1997) 193]. This implies that such corrections could be very important in optical methods of temperature measurement. © 1999 Elsevier Science B.V.

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1. Introduction

Optical methods of temperature measurement are specially important for very fast processes (such as shock waves [1]) and for systems that are very small (such as sonoluminescent bubbles [2] and nanoparticles [3]) or have temperatures too high to be measured by means of contact thermometers (this happens, e.g., in furnaces of steel industries [4] and stellar atmospheres [5]). The Wien displacement law is a well-known method to infer the temperature of a system from the radiation it emits. However, systems such as those mentioned above are usually (if not always) in nonequilibrium states. Thus any description based on the Wien displacement law may be very crude, because this law follows from the *equilibrium* expression for the radiation intensity (i.e., the Planck function) [6]. One way to get around this difficulty is to resort to the classical theory of photon diffusion in near-equilibrium systems. This theory is based on the phenomenological hypothesis of radiative local thermodynamic equilibrium, which is the assumption that the emission coefficient of radiation by matter is approximately the product of the Planck function times the absorption coefficient, and leads to the following result for the intensity of radiation [7,8],

$$\tilde{I}_\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{e^\chi - 1}\left(1 - \chi\frac{e^\chi}{e^\chi - 1}\varepsilon\cos\theta\right), \qquad (1)$$

where h is the Planck constant, c is the speed of light in vacuo, λ the wavelength, θ the angle between the direction of propagation and that of the temperature gradient, and

$$\chi = \frac{hc}{kT\lambda}, \quad \varepsilon = \frac{|\nabla T|}{\sigma T} \qquad (2)$$

are dimensionless quantities, with k the Boltzmann constant, T the temperature and σ the absorption coefficient (here assumed independent of wavelength for simplicity). In Ref. [9], it has been rigorously shown that the physical meaning of ε is that it is a measure of how far away from equilibrium the system is (in thermal equilibrium we have $\varepsilon = 0$). Recently, it has been shown that the intensity (1) yields corrections to

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the Wien displacement that are important enough to be measurable [10]. Eq. (1) has also been derived and generalized without making use of any phenomenological assumption but applying information statistical theory to the case in which radiation interacts with a classical nonrelativistic monatomic ideal gas [9]. This approach is based on the maximization of the entropy density under the constraints of fixed energy density, molecular number density and radiative heat flux, which leads to a radiation distribution of the form

$$\tilde{f}_r = \frac{1}{\exp(\beta p_r c - \boldsymbol{\gamma} \cdot \boldsymbol{p}_r c \boldsymbol{c}) - 1}, \tag{3}$$

where β and $\boldsymbol{\gamma}$ are Lagrange multipliers, p_r is the photon momentum and $\boldsymbol{c}$ its velocity. However, it has been noted [11] that this distribution, already proposed in Ref. [12], can be transformed into an equilibrium distribution by performing a Lorentz boost. This is why the authors of Ref. [11] argued that the distribution (3) does not describe a nonequilibrium system but an equilibrium system as seen by an observer moving relative to it (this relative motion transforms the energy and frequency of photons [1] and gives rise to an energy flux that is therefore purely advective). In order to avoid this problem, they proposed to use an additional constraint of no global motion of the system [11]. This was explicitly done by Domínguez in Ref. [13], who was able to deal with the situation of a nonadvective, purely heat flow by requiring an additional constraint of vanishing photon number flux, namely [2]

$$\boldsymbol{J}_N = \int_{R^3} \frac{\mathrm{d}^3 p_r}{h^3} \boldsymbol{c} f_r = \boldsymbol{0}, \tag{4}$$

which is the radiative analogue to the constraint of vanishing matter number flux used in information theory of nonadvective, purely conductive systems [3]. This analogy, and the fact that Eq. (3) becomes Planckian in a specific frame, are motivations to explore the consequences of the constraint (4), see e.g. Ref. [13]. Another way to introduce this constraint is to note that all measurable quantities should in principle be taken into account in the entropy maximization, but use of $\boldsymbol{J}_N$ would yield an entropy depending on $\boldsymbol{J}_N$, in sharp contrast to the thermodynamics of matter systems [14] unless one requires that $\boldsymbol{J}_N = 0$, as done in Eq. (4). Use of this additional constraint (4) yields [4]

$$f_r = \frac{1}{\exp(\beta p_r c - \boldsymbol{\gamma} \cdot \boldsymbol{p}_r c \boldsymbol{c} + \boldsymbol{\delta} \cdot \boldsymbol{c}) - 1}, \tag{5}$$

where β, $\boldsymbol{\gamma}$ and $\boldsymbol{\delta}$ are Lagrange multipliers (we have chosen the negative sign in front of $\boldsymbol{\gamma}$ in order to make the notation here similar to that in Refs. [9] and [10]). The distribution f_r, given by Eq. (5), is different from $\tilde{f}_r$ (see Eq. (3)), and will therefore lead to a radiation intensity I_λ different from the classical intensity $\tilde{I}_\lambda$ (Eq. (1)). Not only from a conceptual perspective but also because of the practical applications we have summarized at the beginning, it is of importance to determine if such an intensity yields corrections to the generalized Wien displacement, and in case it does, whether they are smaller or higher than those derived in Ref. [10] for the classical intensity $\tilde{I}_\lambda$. Thus, here we will study the vanishing photon flux theory based on Eq. (4) and compare both models.

2. Vanishing photon-flux nonequilibrium systems

For a system composed of matter and radiation, the entropy density can be written as [6]

$$\rho s = \rho s_m + \rho s_r = -k \int_{R^3} \frac{\mathrm{d}^3 p_m}{h^3} F(f_m) + 2k \int_{R^3} \frac{\mathrm{d}^3 p_r}{h^3} [(1 + f_r) \ln(1 + f_r) - f_r \ln f_r], \tag{6}$$

where the subindexes m and r stand for matter and radiation; s, p and f are the corresponding specific entropies, momenta and distribution functions, respectively; and ρ is the matter density. The entropy density (6) has been used in Refs. [9,10] for the specific case such that $F(f_m) = f_m \ln f_m$, which corresponds to a classical ideal gas. Because this is a very special case of matter, whereas optical temperature measurement is important in very different kinds of systems (see

[1] See Eq. (8) in Ref. [11].

[2] See the text under Eq. (13) and p. 7712, as well as Eqs. (8) and (10) in Ref. [13].

[3] Ref. [12], text above Eq. (30).

[4] Ref. [13], Eq. (14).

the applications we have summarized in the first paragraph), here we leave $F(f_m)$ unspecified. We also have the statistical definitions

$$\rho u = \rho u_m + \rho u_r = \int_{R^3} \frac{d^3 p_m}{h^3} H(p_m) f_m + 2 \int_{R^3} \frac{d^3 p_r}{h^3} p_r c f_r , \tag{7}$$

$$\langle A_l \rangle = \int_{R^3} \frac{d^3 p_m}{h^3} A^l(p_m) f_m , \tag{8}$$

$$\boldsymbol{F} = 2 \int_{R^3} \frac{d^3 p_r}{h^3} p_r c \boldsymbol{c} f_r , \tag{9}$$

with u the energy per unit mass and $\boldsymbol{F}$ the radiative heat (or energy) flux. The microscopic operator $H(p_m)$ corresponds to the energy of the matter part (for example, in the special case of nonrelativistic monatomic molecules we would have $H(p_m) = p_m^2/2m$), and A^l are any additional operators.

We make use of information statistical theory [15] by maximizing the entropy density (6) under the constraints (7)-(9) and (4), and finally obtain Eq. (5), which had been previously derived for a purely radiation system [13]. In contrast, here we are considering a system composed of matter in addition to radiation. This will allow us to relate the Lagrange multipliers to directly measurable quantities. By assuming that near-equilibrium states correspond to small values of the radiation multipliers $\boldsymbol{\gamma}$ and $\boldsymbol{\delta}$, a first-order Taylor expansion of the r.h.s. of (5) yields

$$f_r = \frac{1}{\exp(\beta p_r c) - 1} \times \left(1 + \frac{\exp(\beta p_r c)}{\exp(\beta p_r c) - 1} p_r c \boldsymbol{c} \cdot \boldsymbol{\gamma} - \frac{\exp(\beta p_r c)}{\exp(\beta p_r c) - 1} \boldsymbol{c} \cdot \boldsymbol{\delta} \right), \tag{10}$$

which we insert into the constraints (4) and (9). After integration we find

$$\boldsymbol{\gamma} = \frac{\pi^2 \beta}{18 \xi(3)} \boldsymbol{\delta} = \frac{k^4 \beta^5}{4ac^2 (\frac{1}{3} - (135/\pi^6)[\xi(3)]^2)} \boldsymbol{F} , \tag{11}$$

where $\xi(z)$ is the Riemann Zeta function, $a = 8\pi^5 k^4 / 15 c^3 h^3$ is the blackbody constant, and the integrals have been performed by making use of the formulae 3.423,2 and 9.542, 1 in Ref. [16].

By finding out the differential of the specific entropy along the usual procedure (see Appendix A in Ref. [9]), and making use of the thermodynamical definition of temperature T, namely $1/T \equiv \partial s / \partial u$, one finds

$$\beta = \frac{1}{kT} . \tag{12}$$

We assume for simplicity that the system is in a steady state. Then the grey radiative transfer equation (RTE) has the simple form $(\boldsymbol{c}/c) \cdot \boldsymbol{\nabla} I_\lambda = -\sigma I_\lambda + j_\lambda$, which relates the variation of intensity in any direction $\boldsymbol{c}/c$ to the absorption and emission coefficients, σ and j_λ respectively. As in Eqs. (1) and (2), we have assumed σ to be independent of frequency for simplicity (the grey approximation [8,17]). In the special case of equilibrium, I_λ is Planckian with uniform temperature and $\boldsymbol{\nabla} I_\lambda = \boldsymbol{0}$, so that emission and absorption processes compensate each other. Here we are interested in nonequilibrium states ($\boldsymbol{\nabla} I_\lambda \neq \boldsymbol{0}$). As it has been shown previously [18,19], integration of the RTE given above over all frequencies and solid angles yields

$$c \left(\frac{\partial Pxi}{\partial x} + \frac{\partial P_{yi}}{\partial y} + \frac{\partial Pzi}{\partial z} \right) = -\sigma F_i , \tag{13}$$

with $i = x, y, z$, and the pressure tensor of radiation is [8,17] $P_{ji} = 2 \int_{R^3} (d^3 p_r / h^3)(p_r/c) c_j c_i f_r$. It may be easily calculated by insertion of Eqs. (10) and (12) and integration. This yields $P_{ji} = \frac{1}{3} a T^4 \delta_{ji}$, where $\delta_{ji} = 1$ if $i = j$ and $\delta_{ji} = 0$ otherwise. Use of this result and of $\boldsymbol{F}$, given by Eq. (11) into Eq. (13), yields

$$\boldsymbol{\gamma} = - \frac{1}{1 - (405/\pi^6)[\xi(3)]^2} \frac{1}{\sigma c k T^2} \boldsymbol{\nabla} T . \tag{14}$$

The intensity of radiation is related to the photon distribution function through $I_\lambda = (2hc^2/\lambda^5) f_r$ [20]. Thus, making use of Eqs. (10), (11), (12), (14) and (2), and of the fact that the energy of a photon is $p_r c = hc/\lambda$,

$$I_\lambda = \frac{2hc^2}{\lambda^5} \frac{1}{e^\chi - 1} \times \left(1 - \frac{\chi - 18\xi(3)/\pi^2}{1 - (405/\pi^6)[\xi(3)]^2} \frac{e^\chi}{e^\chi - 1} \varepsilon \cos\theta \right), \tag{15}$$

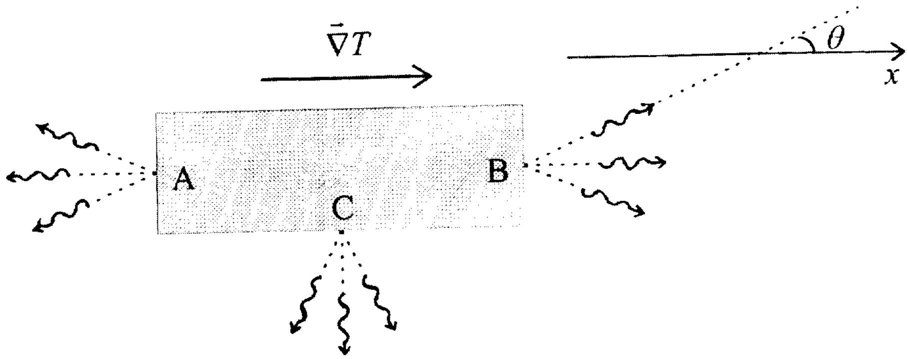

Fig. 1. A matter system with a nonuniform temperature distribution. Here θ is the angle between the direction of propagation and that of the temperature gradient, as illustrated in the figure for a particular photon emitted by the nonequilibrium system. This system generalizes that considered previously (see Fig. 1 in Ref. [10]): the matter part of the system no longer needs to be assumed a classical monatomic, nonrelativistic ideal gas. In Figs. 2 and 3 we illustrate the predictions for the system depicted here, making use of the theoretical model derived in the text.

which differs, as expected, from the result corresponding to the classical diffusion theory (Eq. (1)).

3. The Wien displacement in nonequilibrium systems

We consider a matter system under a temperature gradient (see Fig. 1), and study the radiation it emits. The intensity due to the photons that leave the system through a unit area centered at point B in Fig. 1 is $i_{\lambda B} = \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta \sin\theta \cos\theta \; I_{\lambda B}$, where $I_{\lambda B}$ is given by Eqs. (15) and (2) evaluated at point B, i.e. $T = T_B$ and $\nabla T = \nabla T|_B$. The intensities $i_{\lambda A}$ and $i_{\lambda C}$, corresponding to points A and C in Fig. 1, can be considered analogously [9]. Then, use of Eq. (15) and integration yields

$$i_{\lambda\, l} = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\chi_l} - 1} \times \left(1 + \alpha_l \frac{2\varepsilon_l}{3} \frac{\chi_l - 18\xi(3)/\pi^2}{1 - (405/\pi^6)[\xi(3)]^2} \frac{e^{\chi_l}}{e^{\chi_l} - 1}\right), \tag{16}$$

where $l = A, B, C$; $\alpha_A = +1$, $\alpha_B = -1$, $\alpha_C = 0$; and $\chi_A = hc/kT_A\lambda$, $\varepsilon_A = |\nabla T|/\sigma T_A$, etc. Here we have assumed that the temperature gradient is uniform.

In Fig. 2 we plot the spectra for the case $\sigma = 0.1$ m^{-1} [9], $T_A = 2000$ K, $T_B = 2001$ K, and a temperature gradient of $|\nabla T| = 5$ K/m, as predicted by Eq. (16) (dotted curves). We also include the predictions from classical diffusion theory [7–9] (full curves), which corresponds to Eq. (1) (these predictions are given by, e.g., Eqs. (8)–(10), (4) and (5) in Ref. [10]). The classical and the vanishing-flux theories yield the same predictions for an observer that detects the radiation looking perpendicularly to the direction of the temperature gradient (in fact, Eq. (16) for $l = C$ is nothing but the equilibrium, or Planckian, intensity). By contrast, predictions are different if the direction of observation is that of the temperature gradient (curves A in Fig. 2) or the opposite one (curves B). Fig. 2 shows that the wavelength of maximum intensity $\lambda_{\max}$ is also different: the theory analyzed in Ref. [10] predicts $\lambda_{\max\, B} = 1.47$ μm, which compared to the equilibrium result ($\lambda_{\max\, eq} = 1.45$ μm) yields an effect of about 1.5%. However, for the same system the model presented here predicts $\lambda_{\max\, B} = 1.52$ μm, which yields quite a larger effect, of about 5%.

The wavelength of maximum intensity corresponds to

$$\frac{\partial i_{\lambda A}}{\partial \chi_A} = 0, \quad \frac{\partial i_{\lambda B}}{\partial \chi_B} = 0, \quad \frac{\partial i_{\lambda C}}{\partial \chi_C} = 0. \tag{17}$$

Making use of Eq. (16) into (17) we find quite a complicated equation. However, Eqs. (10) and (16) are valid up to first order around equilibrium so that we may simply make use of the approach corresponding to Eq. (15) in Ref. [10]. This yields

$$\chi_A(\varepsilon_A) = 4.9651 + 8.4851\varepsilon_A, \tag{18}$$

$$\chi_B(\varepsilon_B) = 4.9651 - 8.4851\varepsilon_B, \tag{19}$$

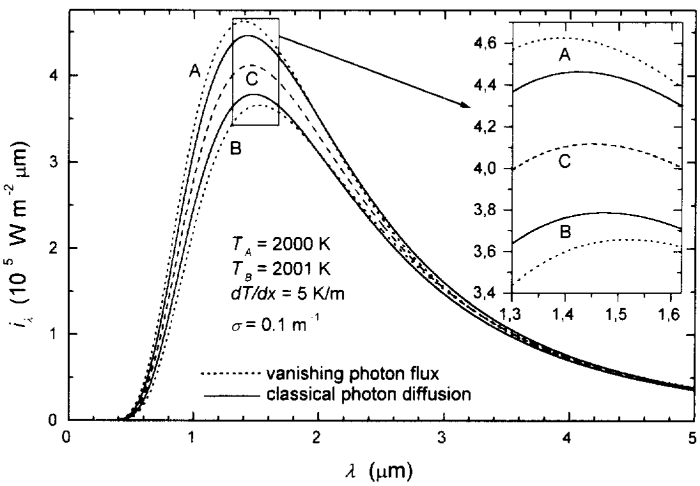

Fig. 2. Comparison between the spectra predicted by the model derived in the present paper (dotted curves) and by the classical theory of photon diffusion (full curves), for the system in Fig. 1. In this figure, the spectra A are those predicted at point A in Fig. 1, etc. The dashed line is a Planckian spectrum (at this scale, one may not distinguish Planckian spectra at temperatures T_A, T_B and T_C), and it is the prediction of both theories for the special case of point C in Fig. 1. The important part of this figure is the inset, which allows us to distinguish the maxima of the spectra (i.e., the generalized Wien displacement).

$$\chi_C(\varepsilon_C) = 4.9651\,. \tag{20}$$

In Fig. 3 we present the predictions for the generalized Wien displacement as a function of the nonequilibrium parameter ε, according to Eqs. (18)-(20) (dotted lines). The predictions of the classical theory [7-9], which were analyzed in Ref. [10], are also included for comparison (full lines). It is seen that, in accordance with the example presented in Fig. 2, the requirement of vanishing photon number flux (which had not been previously taken into account) yields more important corrections than the classical theory. In thermal equilibrium ($\varepsilon = 0$) all intensities are Planckian (see Eq. (16)) and Fig. 3 agrees with the Wien displacement law, namely $\chi = 4.9651$. The higher the value of ε is, the larger the corrections are. In the case of very high temperature gradients, the first-order approximation (10) will break down, and one may carry out the expansion up to higher orders (the second-order extension of the classical photon diffusion theory has been explicitly worked out in Refs. [9,10,21]).

As an application, assume we observe a system with $\sigma = 0.1$ m^{-1} and $|\nabla T| = 10$ K/m and find that its wavelength of maximum intensity is $\lambda_{\max\ A} = 1.4004$ μm. If we want to determine the temperature of the system, we could make use of the equilibrium Wien displacement, i.e. $T_A = ch/4.9651k\lambda_{\max\ A} = 2069$ K. A better alternative would be to make use of the classical theory of photon diffusion, as analyzed in Ref. [10]. This yields $T_A = 2000$ K, so that the error stemming from the equilibrium approximation would be, within classical photon diffusion theory, 3.5% [10]. However, the requirement of a vanishing photon flux leads to a different description. Then, Eqs. (18) and (2) yield $T_A = 1898$ K, so that the error of the equilibrium approximation would be of 171 K or 9%.

4. Conclusions

We have shown that the additional constraint of vanishing photon number flux yields near-equilibrium corrections to the Wien displacement that are much more relevant than those predicted by classical photon diffusion theory. We mention, on the other hand, that in contrast to the claim in Ref. [11], the fact that Eq. (3) becomes Planckian in a given frame does not seem sufficient to conclude that this corresponds to equilibrium radiation: an experimental approach would be not only useful but also important in view of the high differences here computed.

We have made use of the principle of maximum entropy in order to close the set of radiative hydro-

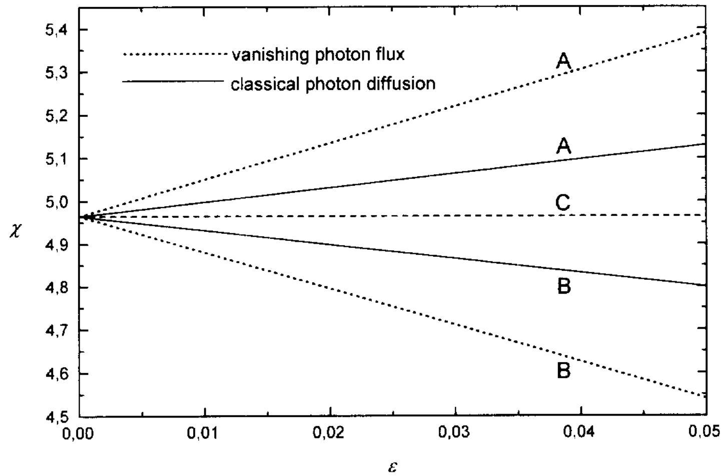

Fig. 3. Predictions for the generalized Wien displacement law, according to the model analyzed here (dotted lines) and to the usual theory of photon diffusion (full lines). The dashed line is the prediction from both theories for the special case of point C in Fig. 1. Since in this case the near-equilibrium spectrum is Planckian, this line corresponds to the equilibrium, or Wien, displacement law.

dynamic equations. Such equations follow from the radiative transfer equation (RTE), which has in turn been derived form first principles in a variety of ways [22-26]. We have here applied the grey RTE for the sake of simplicity, and because it is enough in order to perform estimations, but it is possible to generalize the results for the nonequilibrium intensity without making use of the grey approximation [27].

Although we have considered a mathematically simple description for the system, it can be shown that the result $\beta = 1/kT$ is valid for an arbitrary interaction between the matter particles [28]. This is not surprising since β links the thermal state of matter to its radiative emission. In other words, we have dealt with thermal emission and not with radiation-matter energy equilibration processes [29]. However, in contrast to the case corresponding to the usual, Wien displacement, we have allowed for the possibility of a temperature gradient in the system.

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