

# Radiative Energy Transfer with Filters and Stokes/Anti-Stokes Coatings

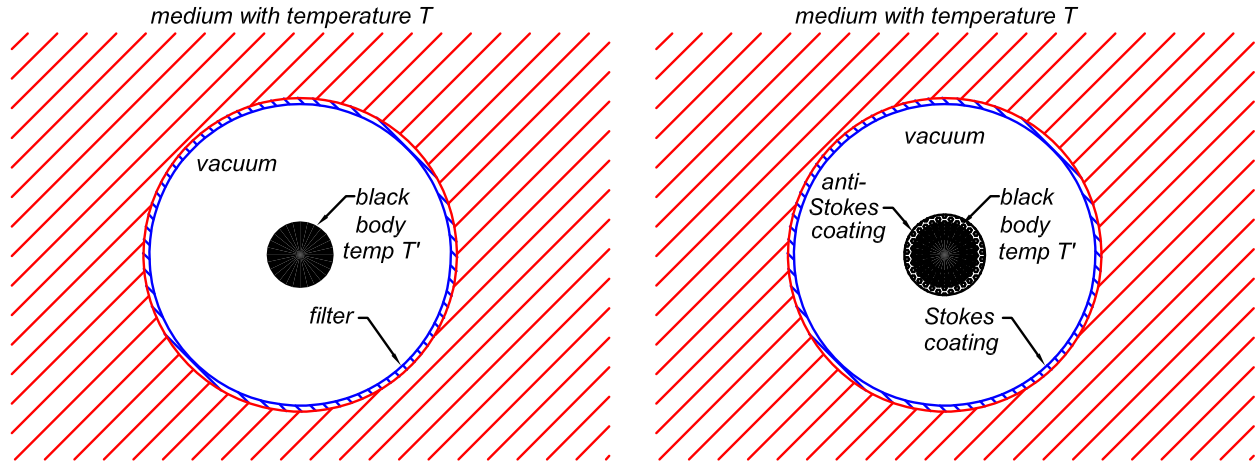
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## 1 Problem

An ideal blackbody resides inside a cavity in a medium (heat bath) of temperature  $T$  that is also an ideal blackbody.<sup>1</sup> If the small black body is initially at temperature  $T$ , could its temperature evolve to an equilibrium temperature  $T'$  different from  $T$  if the inner surface of the cavity were covered with a passive filter? For example, the filter might be an ideal transmitter for light of some wavelengths, while being an ideal blackbody for all other wavelengths (meaning that the filter is perfectly absorbing at the other wavelengths, and emits light with a blackbody spectrum, described by a single “temperature”, at those other wavelengths).



Consider also the case that the interior of the cavity is coated with a Stokes-shift material [2],<sup>2</sup> while the small blackbody inside the cavity is coated with an anti-Stokes-shift material [3, 4], where the emission and absorption spectra of these two materials are complementary.<sup>3</sup>

<sup>1</sup>An ideal blackbody is perfectly absorbing of light at all wavelengths, and emits light (electromagnetic radiation) with the Planck spectrum associated with the temperature  $T$  of the body [1].

<sup>2</sup>Stokes’ term “refrangibility” of light corresponds to its frequency/energy of its photons. That is, greater “refrangibility” means higher frequency/energy.

<sup>3</sup>Shortly after Stokes paper (1852), several people (Emsmann, Akin, Tyndall) considered the possibility that absorption of light of one frequency might be followed by emission of light with a higher frequency. A contentious debate followed into the mid 1860’s, over names (negative fluorescence, calcescence and calorescence) for this phenomenon, as well as claims that it had been observed in the laboratory [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. In these experiments a metal was heated by a flame, or by focused light, until it became hot enough that its glow included light of shorter wavelength than that of the heat source. We would now consider this to be a demonstration that the blackbody-radiation spectrum, at any temperature, contains components with very short wavelengths (while a metal heated by a flame always has a temperature less than or equal to that of the flame).

In 1867, observations were reported [18] of absorption (by  $\text{CaF}_2$  = fluorite/fluor-spar, after which fluores-

*This problem was suggested by Scott Zimmerman.*

## 2 Solution

### 2.1 Cavity Lined with a Filter

We recall that, as first argued by Kirchhoff [23], in the absence of the filter, a blackbody inside a black-walled cavity has the same equilibrium temperature as the cavity.<sup>4</sup>

When the filter (of the type described above) is added, we consider three temperatures in the system, temperature  $T$  of the medium that contains the black-walled cavity, temperature  $T'$  of the blackbody inside the cavity, and temperature  $T_f$  of the filter. We suppose that the latter temperature has the significance that the filter emits (and absorbs) radiation according to the Planck intensity spectrum [1], at the wavelengths for which it is not transparent.

If the filter has temperature  $T_f = T$ , then the inner surface emits (and absorbs) radiation according to the Planck spectrum with temperature  $T$ , part of which is transmitted through the filter from the inner surface of the black-walled cavity, and the remainder of which is emitted by the inner surface of the filter. In this case, the inner surface of the filter behaves like a blackbody with respect to the small blackbody inside the cavity, and hence the latter has equilibrium temperature  $T$ .

To make the problem more interesting, if perhaps somewhat unrealistic, we now suppose that the filter is made of a thermally insulating material, such that its outer surface is at temperature  $T$  (being in thermal contact with the surrounding medium that is at temperature  $T$ ), while its inner surface can be at a different temperature  $T_f$ . However, it is again clear that if the initial temperatures are  $T' = T_f = T$ , then the system will remain in this state, and the  $T$  is an equilibrium temperature.

Could the system also have other equilibrium temperatures (while the surrounding medium remains at temperature  $T$ )?

For example, suppose initially  $T' > T_f > T$ . Then, the small blackbody radiates more energy than it absorbs, and begins to cool down. Some of the energy radiated by the small black body is absorbed by the inner surface of the filter, which therefore begins to heat up. But, as the temperatures evolve, they continue to obey  $T' > T_f > T$  until all three temperatures become equal (to  $T$ ).

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cence was named by Stokes) of radiant heat followed by emission of shorter-wavelength light, which latter had been in some sense been stored in the crystal (perhaps as suggested by the “optical sponge” model of La Galla [19]). This process is now called **thermoluminescence** or **persistent luminescence** (with early reports by Cascariolo [20] using BaS and by Boyle [21] using a diamond; see also p. 399 of [22]) in which a material has been excited into a metastable state by past photon absorption (like a lasing medium), and when heated, phonon-induced transitions promote the metastable states to ones that decay quickly, with emission of higher frequency light. In slight contrast, this sequence happens very quickly in an anti-Stokes-shift process (in which a photon is absorbed to excite an atom, that is quickly further excited by a phonon, permitting emission of a photon of higher energy than of the absorbed photon).

The emerging interest in blackbody radiation [23] was such that further study of the anti-Stokes-shift process lay dormant for 60 years, until [3], while thermoluminescence re-emerged in the 1950’s as a method for dating archaeological objects [24].

<sup>4</sup>This was anticipated by Prevost (1791) in his so-called Law of Exchanges [25, 26, 27, 28]; see pp. 220ff of [29]. Kirchhoff also built on the work of de la Provostaye and Desains [30, 31, 32], and of Stewart [33, 34].

We could also consider the other five scenarios for unequal initial temperatures in the system, but in all cases all the temperatures converge on  $T$ , which is the only equilibrium temperature of the system.

### 2.1.1 Comment

The result that the system under consideration in this section, which is a “passive” system, cannot lead to an equilibrium temperature  $T'$  higher than that of its surrounding environment, appears to agree with one of the earliest formulations of the Second Law of Thermodynamics by W. Thomson, sec. 11 of [35], that net heat will not spontaneously flow from a cooler body to a hotter one, in a “closed” system.<sup>5,6</sup>

## 2.2 Use of Stokes and Anti-Stokes Coatings

Some materials exhibit a Stokes shift (first described in [2]), meaning that they absorb light only within a limited range of wavelengths, and reflect (or transmit) light of other wavelengths, while emitting light of longer wavelength (photons of lower energy) than that absorbed. More rare is the case of an anti-Stokes shift,<sup>7</sup> in which photons are emitted with higher energy (shorter wavelength) than absorbed, as illustrated in the figures below (from [4, 46]).<sup>8</sup>

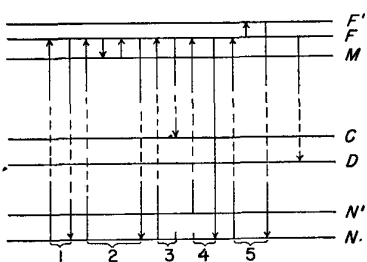
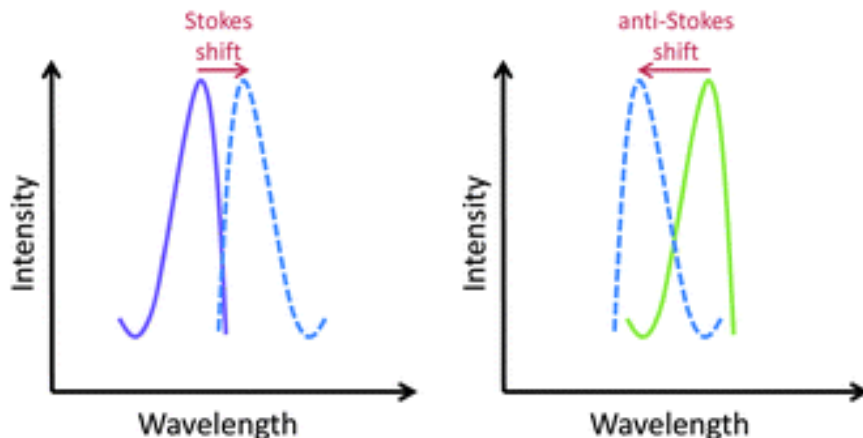


FIG. 1. Energy level diagram for the representation of fluorescence and phosphorescence.

- 1: resonance radiation.
- 2: phosphorescence.
- 3: fluorescence.
- 4 and 5: anti-Stokes fluorescence.



<sup>5</sup>This “law” does not hold for an “open” system. For example, sunlight can be focused on a small object on the Earth to bring it to a temperature hotter than the Sun, in that very little radiation from the hot object is intercepted by the Sun (which does not enclose the object/Earth). Another example of an “open” system is a Stokes-shift material that absorbs sunlight, and emits preferentially in the atmospheric “window” around 10- $\mu\text{m}$  wavelength, to achieve passive cooling [36, 37, 38, 39].

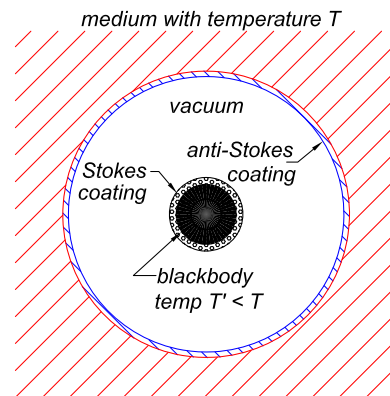
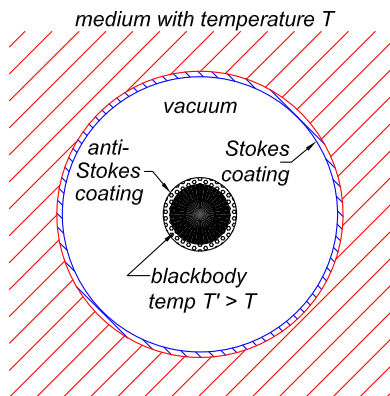
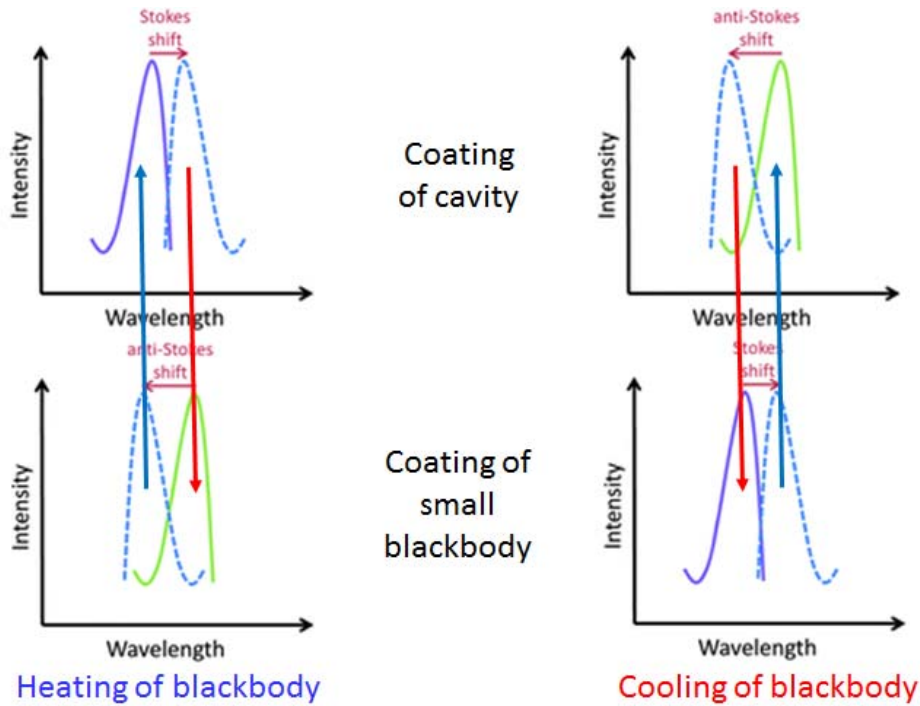
The “law” also does not hold for “active” systems, such as fires and other chemical reactions, electrical heating, refrigerators (consideration of which by Carnot [40, 41] inspired Thomson [35] and Clausius [42, 43]), Maxwell’s demon (pp. 213-214 of [44], p. 308 of [29]), lasing materials, *etc.* *A proposal for a 3-level-maser refrigerator was made in 1959* [45].

<sup>6</sup>If the small blackbody in the present example were made of the same material as the filter, then an equilibrium could exist with  $T' = T_f \neq T$ , since in this case the filter and small body interact with one another radiatively, but neither the small body nor the inner surface of the filter interact with the portion of the radiation from the surrounding medium that enters the cavity through the filter.

<sup>7</sup>Stokes’ great paper [2] was followed by suggestions from various people that there might also exist processes in which the emitted light has higher frequency/energy than that of the light absorbed.

<sup>8</sup>Both fluorescence and phosphorescence of types 1 and 2 in the left figure are Stokes-shift processes.

Suppose we coated the interior of the cavity with a Stokes-shift material, and coated the small blackbody with an anti-Stokes-shift material, as illustrated in the righthand figure on p. 1. We also suppose that the emission spectrum of the anti-Stokes coating matches the absorption spectrum of the Stokes coating, and *vice versa*. And, we suppose that the central wavelength of the emission spectrum of the Stokes-shift coating on the cavity corresponds to the central wavelength of the Planck spectrum for temperature  $T$ , the temperature of the surrounding medium (heat bath) with the cavity.



Then, the photons absorbed by the Stokes-shift coating on the small blackbody have typical temperature  $T$ , which tends to become the temperature of the small blackbody on which this coating resides. However, that coating emits photons of lower energy than those absorbed, and these photons are subsequently absorbed by the anti-Stokes-shift coating on the cavity, and hence do not return to the small blackbody, as shown in the left side of the figure on the next page. As such, the temperature of the small blackbody rises due to this

(irreversible) cycle of radiative energy transfer,<sup>9</sup> and its equilibrium temperature  $T'$  is higher than that of the surrounding heat bath,  $T' > T$ .<sup>10</sup>

Alternatively, we might suppose that the anti-Stokes-shift coating is on the surface of the cavity, and the Stokes-shift coating is on the small blackbody, which leads to the latter becoming cooler<sup>11</sup> than the former,  $T' < T$ .<sup>12</sup>

### 2.2.1 Anti-Stokes Shift and the Second Law of Thermodynamics

In sec. 2.1.1 we noted that it seemed agreeable to say that the null result of sec. 2.1 was required by the second law of thermodynamics. But, a naïve application of that law to the example of sec. 2.2 also seems to imply that the small body and the surrounding heat bath must be at the same temperature.

A debate on this issue in the 1940's [49, 50, 51] was best resolved by Landau [52] who noted that in examples with radiative heat transfer one must be careful to account for the entropy of the electromagnetic radiation, which is always positive. Indeed, in the present example, the positive increase of the entropy of the light inside the cavity more than compensates for the decrease in the entropy of the heat bath and small blackbody when the temperature of the latter is driven above the former for the case of a Stokes-shift coating on the cavity surface and an anti-Stokes shift coating on the small blackbody (and when the temperature of the latter is driven below the former for the case of an anti-Stokes-shift coating on the cavity surface and a Stokes-shift coating on the small blackbody).<sup>13</sup>

Landau also noted that as the energy difference between absorption and emission increases for an anti-Stokes-shift coating, the rate of energy transfer across this coating decreases.

### 2.2.2 Practicalities

While in principle the use of Stokes/anti-Stokes-shift coatings can permit a blackbody inside a cavity in a heat bath to have an equilibrium temperature different than that of the bath, this process will be weak in practice for a room-temperature heat bath, for which the central wavelength of the associated Planck spectrum is about 10  $\mu\text{m}$ , whereas practical anti-Stokes-shift coatings operate at optical and near infrared wavelengths.<sup>14</sup>

If the heat bath is to be energized by sunlight, it may be better to omit the heat bath, and have the sunlight shine directly on the coating of the cavity that contains the blackbody that is to be heated or cooled.

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<sup>9</sup>This Stokes/anti-Stokes process might be called “evaporative photon heating”.

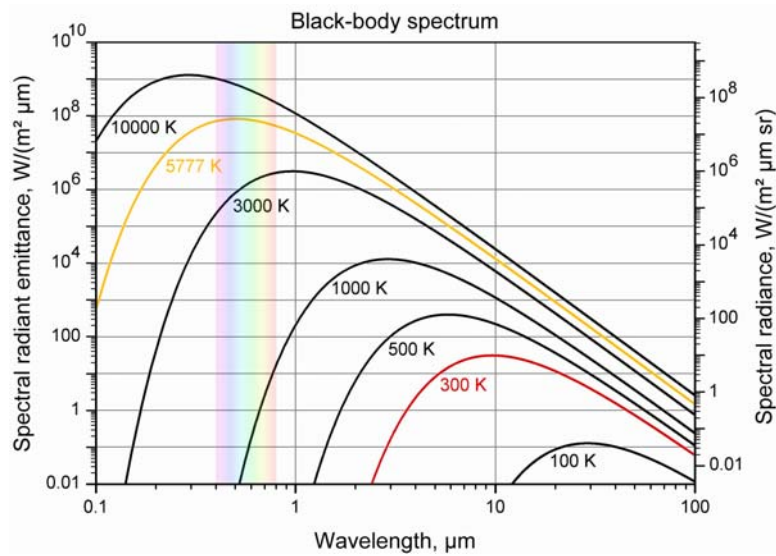
<sup>10</sup>An earlier discussion of this topic by the author, in sec. 2.7 of [47], was insufficiently insightful.

<sup>11</sup>Via “evaporative photon cooling”.

<sup>12</sup>This result is implied in [48], as remarked by E. Yablonovitch (private communication).

<sup>13</sup>The case of cooling of the small blackbody inside the cavity is closely related to laser cooling of solids [53, 54, 55, 56], which concept was anticipated by Pringsheim in his 1929 paper [3]. Discussions of the thermodynamics of laser cooling are given in [57, 58].

<sup>14</sup>The first reported optical refrigerator using anti-Stokes-shift coatings may be that of [59], where cooling by 0.6° C was achieved.



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