Statistical mechanics and Thermodynamic equilibrium. Part 1

- Quick brush-up on free energy and chemical potential.
- Thermodynamic equilibrium.
- Statistical vs. thermodynamic equilibrium of photons: Wien equilibrium and unavoidability of emission/absorption.
- Radiation temperature definions.
- Kinetic equilibrium of matter.
- Radiative equilibrium matter/radiation.

Reference book: Luciano Nobili, *Processi Radiativi ed equazione del trasporto nell'Astrofisica delle alte energie*, Cleup Editrice, Padova, 2002

Quick brush-up on chemical potential

Most of us learned at school, that every physical system tends to minimize its energy. In reality, a many body system tries to decrease its energy and additionally tries to reach a state with maximum disorder. So, it was introduced the so called “Gibbs free energy”, a thermodynamic potential used to calculate the maximum amount of work, other than pressure-volume work, that may be performed by a thermodynamically **closed** (no particles from outside) system at constant temperature and pressure:

G(P,T) = U+PV-TS (S=entropy, U=internal energy, V=volume, P= pressure).

Statistical mechanics, quantum and classical, says that such a system always tries to minimize its free energy, so there is a competition between minimizing energy and maximizing disorder.

When the system reaches a minimum of G, it is in thermodynamic equilibrium, a stationary state where all his macroscopic variables don't change in time as long as it stay isolated.

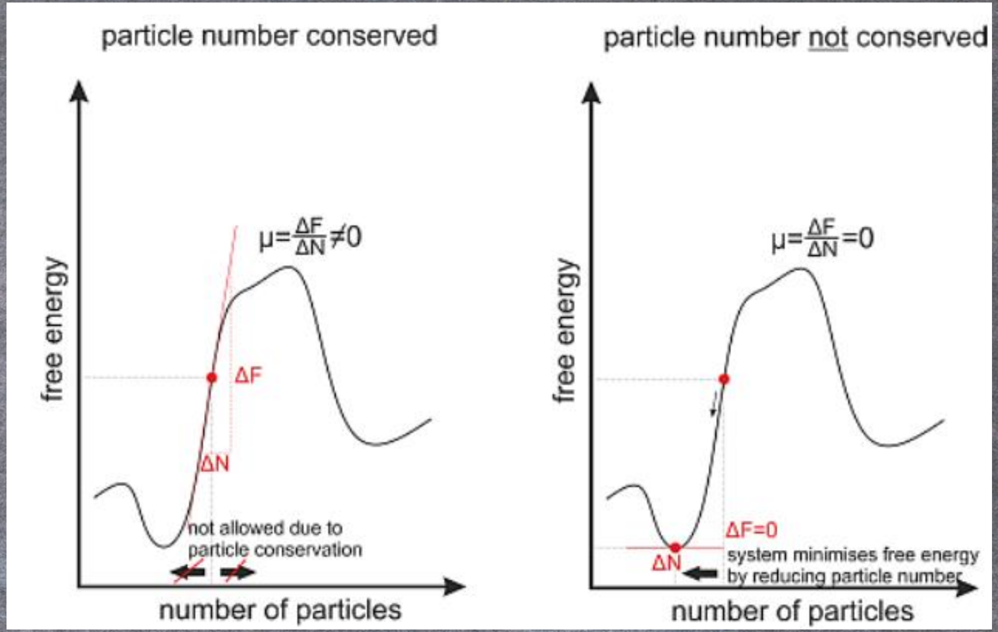
For a system in thermodynamic equilibrium, the chemical potential μ states by how much the free energy will change when we add one additional particle into the system:

$$\mu \equiv \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

In a system where the particle number stays constant over time, as in a gas of atoms, the chemical potential µ will take an arbitrary value depending on the parameters (temperature, pressure) of the gas.

Quick brush-up on chemical potential

But for a photon gas, the number of particles is easily changed by absorption and emission: the system will choose the particle (photon) number in such a way to minimize free energy: being μ the derivative of G w.r.t. N , it will be zero at the minimum of G, that is, at the thermal equilibrium of the photon gas !



Now, ask yourself:
why Fermions do have positive chemical potential, while for Bosons it is negative? Is the above figure describing a classical or quantum system?

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Thermodynamic equilibrium

Two physical systems are in *thermodynamic equilibrium* if there is no net macroscopic flows of *matter* nor of *energy* between them when they are connected by a path permeable to heat. In a system in its own state of thermodynamical equilibrium, no change occurs in its macroscopic properties (U,S,T,etc). Systems in mutual thermodynamic equilibrium are simultaneously in mutual thermal, mechanical, chemical, and radiative equilibria.

Thermal equilibrium: no net flow of thermal energy. (the energy contained in a system that is responsible for its temperature). A part of a system is in thermal equilibrium *with itself* if the **temperature** within it is spatially uniform and temporally constant: we say it is in LTE.

Radiative equilibrium: the total thermal radiation leaving an object is equal to that entering it (a thermal eq. may also be non radiative, e.g. conduction or convection can bring to thermal eq. without involving radiation).

Mechanical equilibrium: no net force on a body.

Chemical equilibrium: concentration of products and reactants do not change in time.

Thermodynamic equilibrium

At thermodynamic equilibrium:

- Entropy S is maximum for an isolated system (U and V are constant);
- U is minimum for a system with constant S,V.
- Helmotz free energy F=U-TS is minimum for a closed system with constant T,V ;
- Gibbs free energy G=F+PV is minimum for a closed system with constant T,P;

Closed system: can exchange energy, but not matter with the environment.

Isolated system: cannot exchange energy nor matter.

Introduction

From the thermodynamical point of view, matter and radiation, even when they share the same space region, form **two distinct systems** in **mutual interaction**. **Each of them can be, separately, in equilibrium or out of equilibrium**.

Generally, the characteristic timescales to reach the equilibrium are shorter for the matter component. Even in presence of strong density and temperature gradients, particles mantain a local distribution very close to the Maxwell-Boltzmann, and their atoms are excited to equilibrium levels. In these cases, the system is said to be in Local Thermodynamic Equilibrium (LTE). LTE is thus indicating **matter in thermodynamic equilibrium** (NOT necessarily with radiation).

We will now discuss equilibrium (and non equilibrium) of radiation and matter separately. Then we will study their mutual interactions.

We already saw that, in mutual thermodynamic equilibrium of matter and radiation in an isolated system (as the Blackbody cavity of the Kirchhoff's experiment), the **matter** source function is $\frac{j_\nu}{\alpha_\nu} = B_\nu(T)$ and that the **radiation** brightness is $I_\nu = B_\nu(T)$.

However, in real situations, we are far from a perfect thermalization between the two systems, as no real body is a perfect absorber/emitter. Furthermore, we usually have to deal with open systems, where energy (mostly in the form of radiation) or even matter, can be exchanged with the environment, preventing the thermodynamic equilibrium between matter and radiation. We can, in such cases, reach a **bolometric** radiative equilibrium: when the radiation is illuminating a given body in LTE, we will see how the emitted thermal has a spectrum which can be much different from the Blackbody one.

Statistical vs. thermodynamic equilibrium of photons

Wien equilibrium

We have seen that, when radiation is thermodynamic equilibrium with matter (also in equilibrium at temperature T), the photon's distribution is isotropic, with average occupation number given by:

$n_\nu^P = \left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}$ (Bose-Einstein statistics with a limiteless number of particles, chemical potential = 0). (*)

The corresponding spectral law, accounting for the number of states of frequency ν, is the Planck distribution: $\frac{dn^P}{d\nu} = \frac{8\pi}{c^3} \frac{\nu^2}{\exp\left(\frac{h\nu}{kT}\right)-1}$

This differs from that of Fermions in equilibrium $n_\nu = \left[\exp\left(\frac{E-\mu}{kT}\right) + 1\right]^{-1}$ for the + sign and for the absence of the chemical potential; $\mu=0$ is a consequence of the non conservation of the photon number. As the photons approach the equilibrium, those in excess are rapidly absorbed. Viceversa, if there's a lack of photons w.r.t. the distribution predicted by the quantum laws, more photons are created. The equilibrium is reached when $\mu=0$ and the photons are distributed among the frequency spectrum according to the Planck distribution.

The rapidity with which radiation comes to equilibrium is only partially dependent on the efficiency of *energy* exchange between photons and matter. Indeed, thanks to the fact that photons can easily be created or destroyed, an important role is that of absorption and emission: whithout them, it would be impossible to satisfy, e.g., equation (*), which relates the photon *number* to the temperature. Indeed, scattering processes (elastic, like Thomson by electrons, Rayleygh or Mie, or anelastic, like Compton and Raman scattering) do NOT change the photon number.

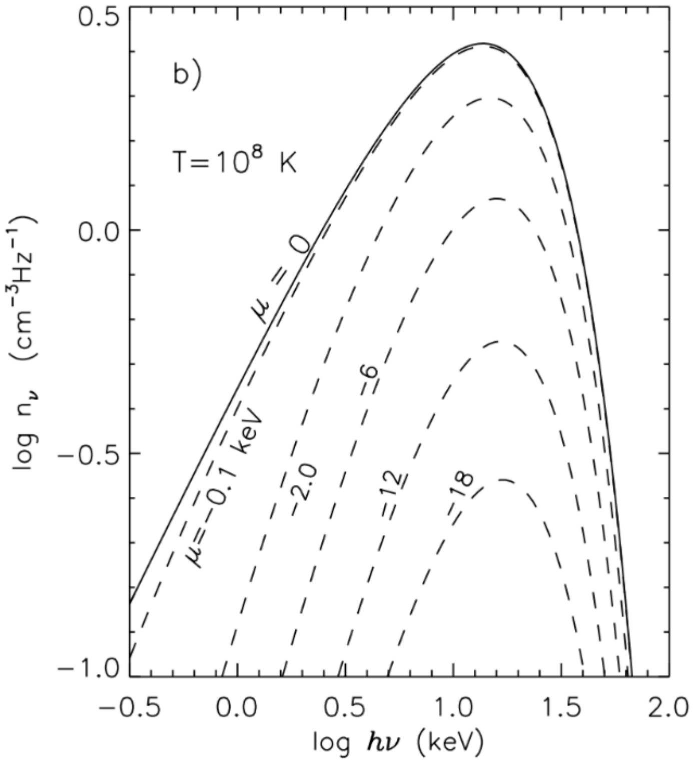
In particolar conditions of temperature and density, very common in rarefied, hot astrophysical plasmas, it may happen that the the photon's formation and destruction mechanisms are unimportant, or that they happen on timescales much longer than the diffusion timescale.

In those cases, it is still possible that, thanks to the Compton interactions, the energy exchange are sufficiently effective to keep the radiation component in a *statistical equilibrium* ($\mu \neq 0$) with matter; but they are not able to bring photons to a *complete thermodynamical equilibrium* ($\mu = 0$). This peculiar situation occurs because diffusion alone keeps the photon number unchanged. Unable to adjust themselves to the Planckian distribution, photons will tend to an isotropic distribution with average occupation number given by the usual Bose-Einstein distribution for Bosons:

$$n_\nu(\mu) = \left[\exp\left(\frac{h\nu-\mu}{kT}\right) - 1\right]^{-1} \quad , \quad \text{with spectral law } \frac{dn}{d\nu} = \frac{8\pi}{c^3}\frac{\nu^2}{\exp\left(\frac{h\nu-\mu}{kT}\right)-1} \qquad \text{and energy density } u(\mu) = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3 d\nu}{\exp\left(\frac{h\nu-\mu}{kT}\right)-1} \ .$$

For a given temperature, the chemical potential is then solely determined by the occupation number (or, equivalently, by the energy density of the photons). It is always negative, and it increases for increasing photon number.

From the figure, we see that as $\mu \longrightarrow 0, n_\nu$ approaches the true value of equilibrium with matter. The difference w.r.t. the Planck distribution is enhanced in the energy range corresponding to low-energy photons, which, as bosons, tend to condensate on their quantum states. When the photon density is much lower than that predicted by the Planck law for that temperature, the chemical potential is $\mu \ll 0$ and the radiation is said to be in **Wien equilibrium**. In this case, the energy distribution becomes similar to the Maxwellian distribution of relativistic particles:



$$n = 16\pi\left(\frac{kT}{hc}\right)^3 e^{\frac{\mu}{kT}} \quad ; \quad \frac{dn}{dx} = \frac{n}{2}x^2e^{-x} \qquad \left(x \equiv \frac{h\nu}{kT}\right)$$

Unavoidability of emission/absorption: a *Gedankenexperiment.*

It is important to specify the role of the chemical potential in a photon gas. A general property of the thermodynamical systems is that **the particle density determines the value of μ** . There is no upper limit to the number of photons that can simultaneously occupy the same quantic state. And, mostly important are the **creation/destruction** processes, **unavoidable in all the radiative processes.** They help radiation to reach complete thermodynamical equilibrium, thanks to the *energy* exchange, but also opportunely modifying the total *number* of photons. The gradual evolution of the distribution function ceases when the codition $\mu = 0$ is reached.

To better clarify this important property, suppose to realize an empty cavity, with walls kept a temperature T. Suppose it is possible to cover the walls of the cavity with an (ideal) completely reflective material, which cannot emit or absorb photons, but only exchange energy. Put inside the cavity a number n of photons , with $n \ll n^P(T)$, and initially distributed on the energy levels in arbitrary way.

Thanks to the interactions with the walls, the radiation evolves to the **statistical equilibrium** (constant temperature), while the number of photons is unchanged. Now, suppose to gradually increase n by entering new photons through a small pierce in the wall. The chemical potential, initially very negative, increase up to 0 when $n = n^P(T)$ and the distribuition becomes that of the **thermodynamical equilibrium**. What happens if we try to increase n now? The chemical potential cannot become positive (n_ν (μ) and u(μ)) would be infinite for $h\nu=\mu>0$.). Thus, every attempt to introduce new photons into the cavity *must fail*. We have to conclude that, in the matter-radiation interaction, adequate processes forbid n to overcome the equilibrium value n^P. In other words, the hypothesis of *the existence of pure diffusion is inconsistent with the statistical laws of bosons*.

Of course, the time needed for μ reaching the value 0, may become very long, for example decreasing the number of absorbers/emitters. But the conclusion is that **absorption/emission by matter are necessary** for the radiation to reach thermodynamical equilibrium (i.e. a Planck distribution).

Radiation temperature definitions

Blackbody radiation is in thermodynamic equilibrium, with a definite value of T. In a general radiation field with arbirary spectrum, the *non-equilibrium prevents us to define a unique temperature value.*

- One way to characterize brightness (specific intensity) at a certain frequency is to give the temperature of the blackbody having the same temperature at that frequency. That is, for any I_ν, we define the brightness temperature $T_b(\nu)$ by the relation $I_\nu = B_\nu(T_b)$. In general, every frequency will correspond to a different brightness temperature (fig, 1). T_b is mostly used in radioastronomy, because at radio frequencies it is directly related to the flux thanks to the Rayleigh-Jeans approximation for low frequencies: $\boxed{I_\nu = \frac{2\nu^2}{c^2}\ kT_b}$. So, it is generally calculated by fitting to a Planckian only the low frequency part of the spectrum (fig. 2).
- The effective temperature is based on the comparison between the total observed flux and that equivalent to a blackbody (fig.3).
- The colour temperature is defined by doing a best fit between the oserved spectrum and a blackbody distribution (fig.4).

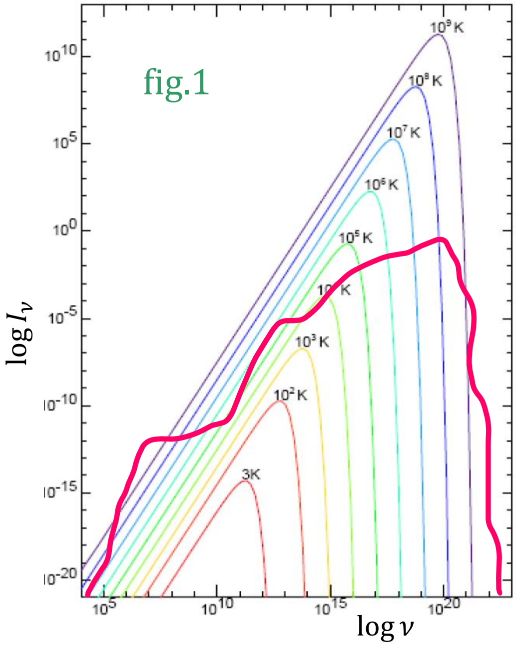


fig.1

fig.2 Brightness temperature

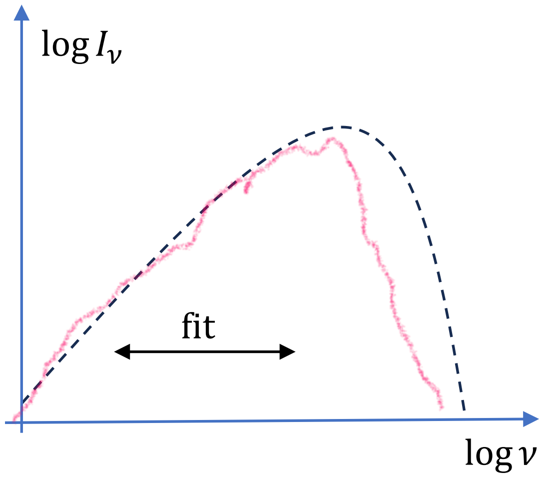


fig.3 Effective temperature

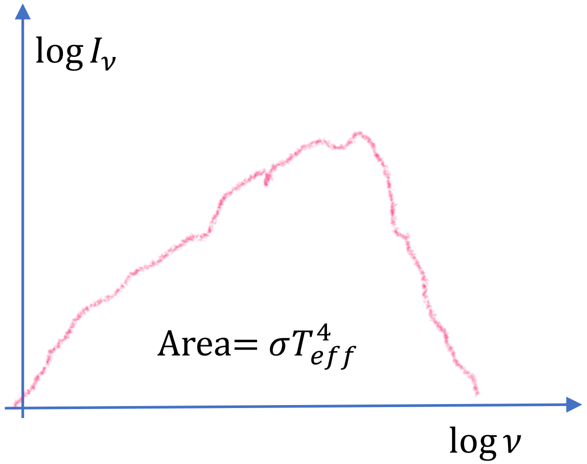
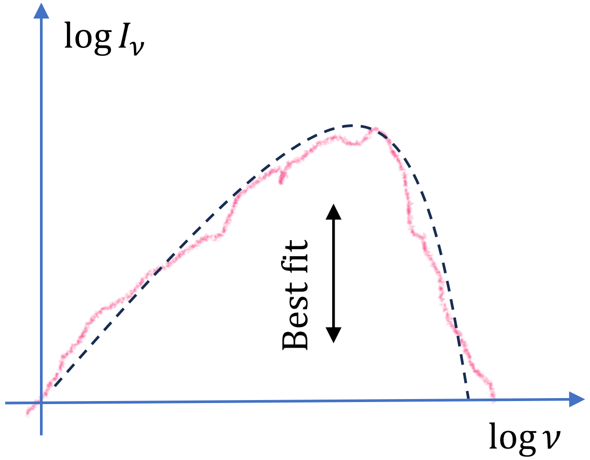


fig.4 Colour temperature



Kinetic equilibrium of matter

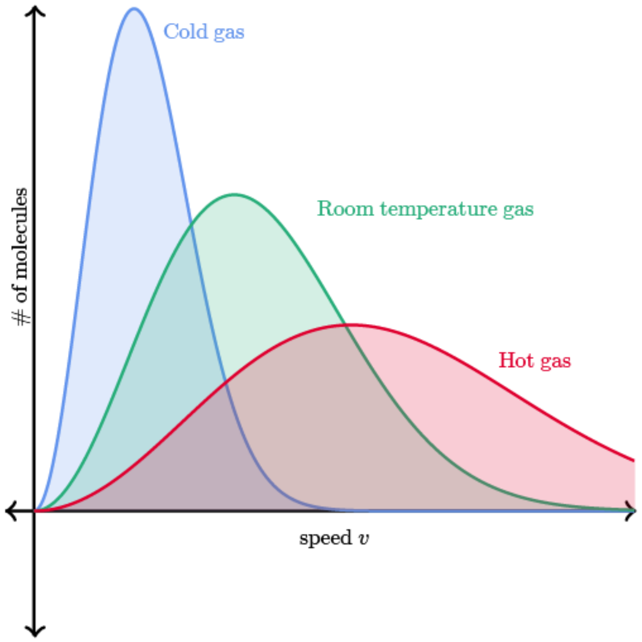
For matter in thermal equilibrium at a certain temperature, the **Maxwell-Boltzmann equation** defines the statistical distribution of particle speeds, derived by equating particle energies with kinetic energy. This is a result of the kinetic theory of gases. For an ideal gas of **point particles**, (no internal structure and no interactions between particles) the energy of each molecule consists only of **translational** kinetic energy, $E=\frac{1}{2}mv^2$. It obeys the equipartition theorem, which assigns an average energy of $\frac{1}{2}kT$ to each degree of freedom . It doesn't count any additional internal degree of freedom where energy can be (vibrational or rotational motions of molecules, etc). (*)

For a system containing a large number N of non-interacting, non-relativistic classical point particles of mass *m* in thermodynamic equilibrium at temperature T, the number of the particles with velocity (in module) between v and v+dv is

$$n(v)dv = \frac{4\pi N}{V}\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv \qquad \text{with } N/V = \text{number of particles per unit volume.}$$

Its validity is limited by quantum mechanics, as the concept of trajectory lose its meaning because of uncertainty principle. Maxwell–Boltzmann distribution is valid when the average distance between particles, d, is large w.r.t. the quantum uncertainty in particle position, $\Delta x \ll d$. For lower distances, the particles become indistinguishable in quantum mechanics. Since $\Delta p_x \Delta v_x \geq \hbar/2$ …., with some algebra one can show the Maxwell–Boltzmann distribution holds for low particle concentration and for high particle mass and T:

$$\left(\frac{N}{V}\right)\frac{\hbar^3}{8(mkT)^{3/2}} \ll 1$$



Otherwise, then the appropriate statistic must be used (Fermi-Dirac or Bose-Einstein).

(*) **Also internal degrees of freedom obey the equipartition theorem. We will see them in Part 2 of these lectures.**

The process of conversion of thermal (kinetic) energy into electromagnetic energy is the thermal radiation. Thermal energy is the kinetic energy of random movements of atoms and molecules in matter. All matter with a nonzero temperature is composed of particles with kinetic energy. These atoms and molecules are composed of charged particles, i.e., protons and electrons. The kinetic interactions among matter particles result in charge acceleration and dipole oscillation. This results in the electrodynamic generation of coupled electric and magnetic fields, resulting in the emission of photons, radiating energy away from the body.

Matter out of equilibrium.

Although Kirchoff's law has several applications, often matter is found out of internal equilibrium. In some cases, a high rarefaction state of the gas, and the presence of high temperatures caused by intense dissipative processes, may increase the timescale for the interaction (e.g. collisions) between the particles. **The kinetic equilibrium cannot be reached in short times.**

These situations are complicated by the fact that the emission and absorption coefficients are no more related by Krchhoff's law.

E.g. Astrophysical plasmas, often composed by several distinct phases, not necessarily in equilbrium. The timescale for Coulombian interaction between charges becomes too large to have an equilibrium between these particles.

Radiative equilibrium matter/radiation

The monodirectional transfer equation can be rewritten, rearranging the terms:

$$\frac{d\,I_\nu}{ds} = \underbrace{\alpha_\nu^{abs}\, S_\nu}_{+E_{\text{emitted}}} + \underbrace{\alpha_\nu^{sc}\, J_\nu}_{\substack{+E_{\text{ conveyed}} \\ \text{into the beam}}} - \underbrace{\alpha_\nu^{abs}\, I_\nu}_{-E_{\text{absorbed}}} - \underbrace{\alpha_\nu^{sc}\, I_\nu}_{\substack{-\ E_{\text{scattered}} \\ \text{out of the beam}}} = \mathrm{dE/\ dA\ ds\ d\Omega\ dt\ d\nu} = \mathrm{dE/\ dV\ d\Omega\ dt\ d\nu}$$

$$\frac{d\,E}{dt d\nu dV} = \frac{d\,I_\nu}{ds}\,\mathrm{d\Omega} = \left(\alpha_\nu^{abs}\, S_\nu + \alpha_\nu^{sc}\, J_\nu - \alpha_\nu^{abs}\, I_\nu - \alpha_\nu^{sc}\, I_\nu\right)\mathrm{d\Omega} \qquad (^{**})$$

We assumed, for simplicity, that the scattering efficiency is isotropic and coherent (it doesn't change the frequency of photons when they are scattered). Integrating over all the solid angle, we already found (Lecture 1) that, in time dt, the specific power conveyed from all directions on the volume element equals the energy scattered by the same element over the solid angle:

$$\int \alpha_\nu^{sc}\, J_\nu\ \mathrm{d\Omega} = 4\pi\, \alpha_\nu^{sc}\, J_\nu = 4\pi\ \alpha_\nu^{sc} \cdot \frac{1}{4\pi}\int I_\nu\ \mathrm{d\Omega} = \alpha_\nu^{sc} \cdot \int I_\nu\ \mathrm{d\Omega}$$

Therefore, integrating eq. (**) w.r.t. the solid angle, we see that the energy balance of a body immersed in a radiation field is *only* due to absorption and emission, not to scattering:

$$\frac{d\,E}{dt d\nu dV} = \int \alpha_\nu^{abs}\, S_\nu\ \mathrm{d\,\Omega} - \int \alpha_\nu^{abs}\, I_\nu\ \mathrm{d\,\Omega}$$

and the **bolometric** equation is

Power emitted   Power absorbed from the incident field

$$\frac{d\,E}{dt\ dV} = \int \alpha_\nu^{abs}\, S_\nu\ \mathrm{d\,\Omega\ d\nu} - \int \alpha_\nu^{abs}\, I_\nu\ \mathrm{d\,\Omega\ d\nu} \quad \Rightarrow \ \textit{Net power P in a volume dV} = \left(\int \alpha_\nu^{abs}\, S_\nu\ \mathrm{d\,\Omega\ d\nu} - \int \alpha_\nu^{abs}\, I_\nu\ \mathrm{d\,\Omega\ d\nu}\right)$$

- If the matter is in **thermal equilibrium** at a temperature $\mathrm{T}_{\text{matter}}$, its source function is $S_\nu = B_\nu(\mathrm{T}_{matter})$. Furthermore, for the matter be in thermal, the radiative equilibrium, the net total power must balance to zero. If we talk about total power, this is a **bolometric radiative equilibrium.**

Radiative equilibrium matter/radiation

$Net\ power\ P\ in\ a\ volume\ dV = (\int \alpha_\nu^{abs}\, B_\nu(\mathrm{T}_{matter})\mathrm{d}\,\Omega\,\mathrm{d}\nu - \int \alpha_\nu^{abs}\, I_\nu\,\mathrm{d}\,\Omega\,\mathrm{d}\nu\,) = 0$ for matter in thermal, radiative equilibrium.

For each volume element of matter in thermal equilibrium embedded in a radiation field I_ν ,

$\Rightarrow \int \alpha_\nu^{abs}\, B_\nu(\mathrm{T}_{matter})\,\mathrm{d}\,\Omega\,\mathrm{d}\nu = \int \alpha_\nu^{abs}\, I_\nu\,\mathrm{d}\,\Omega\,\mathrm{d}\nu$

Power spontaneously emitted by matter in thermal equilibrium (Thermal radiation)

Power absorbed by matter out of the incident radiation field

Notice that:

1) The radiation field doesn't need to be isotropic. $I_\nu = I_\nu\,(\Omega)$

2) The radiation field doesn't need to be in equilibrium itself, i.e., I_ν is not necessarily a Planck function.

3) We assumed the matter in thermal equilibrium, and for thermal emission we know that $S_\nu = B_\nu(\mathrm{T}_{matter})$;

4) Once the matter reaches local thermal, radiative equilibrium, the net power balance on the volume element must be zero.

5) We assumed isotropic coherent scattering, which does not affect the thermal balance, as we have shown.

6) Matter can reach thermal equilibrium even if the incident radiation field is not in equilibrium $(I_\nu \neq B_\nu(\mathrm{T}_{rad}))$. The matter equilibrium temperature will be, however, dependent on the value of I_ν .

Radiative equilibrium matter/radiation

Define the dimensionless absorption efficiency as $Q_{abs}(\nu) \equiv \frac{\alpha_\nu^{abs}}{n\pi a^2} = \frac{\alpha_\nu^{abs}}{n\sigma_{geom}}$ (σ_{geom} geom. cross section of absorbers, n number density) ,

$$\cancel{n\pi a^2} \int \underbrace{\boxed{Q_{abs}(\nu) B_\nu(T_{matter})}}_{\text{Radiated spectrum}} \, d\Omega \, d\nu = \cancel{n\pi a^2} \int Q_{abs}(\nu) \underbrace{\boxed{I_\nu}}_{\text{Incident spectrum}} \, d\Omega \, d\nu$$

Notice that:

7) The frequency spectrum of the emitted radiation is $Q_{abs}(\nu) B_\nu(T_{matter})$, generally different from the spectrum of the incident radiation, $I_\nu(\Omega)$.
This fact is at the basis of the one of the main properties of cosmic dust, where $\alpha_\nu^{abs} \propto \nu^\beta$ with $\beta \sim$1-2 .

8) If the radiation is itself in equilibrium at temperature T_{rad} its intensity is given by the (isotropic) Planck function $B_\nu(T_{rad})$. Matter and incident are, in this case, in thermal equilibrium, because the radiative equilibrium condition becomes:

$$\int Q_{abs}(\nu, \text{Tmatter}) B_\nu(T_{matter}) \, d\Omega \, d\nu = \int Q_{abs}(\nu, \text{Tmatter}) B_\nu(T_{rad}) d\Omega \, d\nu \quad \Rightarrow \boldsymbol{T_{matter} = T_{rad}}.$$

If Q_{abs} (α_ν^{abs}) is a constant (<1), independent on frequency, the radiated spectrum is a rescaled version of the Planck function (*grey body*).

If $Q_{abs} = 1$ ($=Q_{em}$), the radiated spectrum is the same as the incident one, $B_\nu(T)$. Such matter radiator *is* a blackbody.

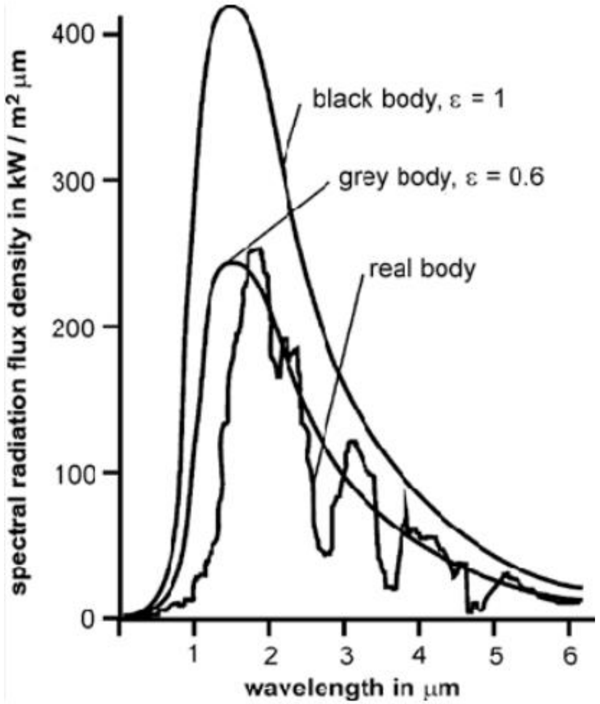
Do not confuse a «blackbody» (matter which absorbs and re-emits as $B_\nu(T_{mat})$ all the incident radiation, anyhow the latter is spectrally distributed, possibly distorting the incident spectrum), with «blackbody radiation» (radiation field spectrally distributed as $B_\nu(T_{rad})$ thanks to a previoulsy acquired thermodynamical equilibrium).

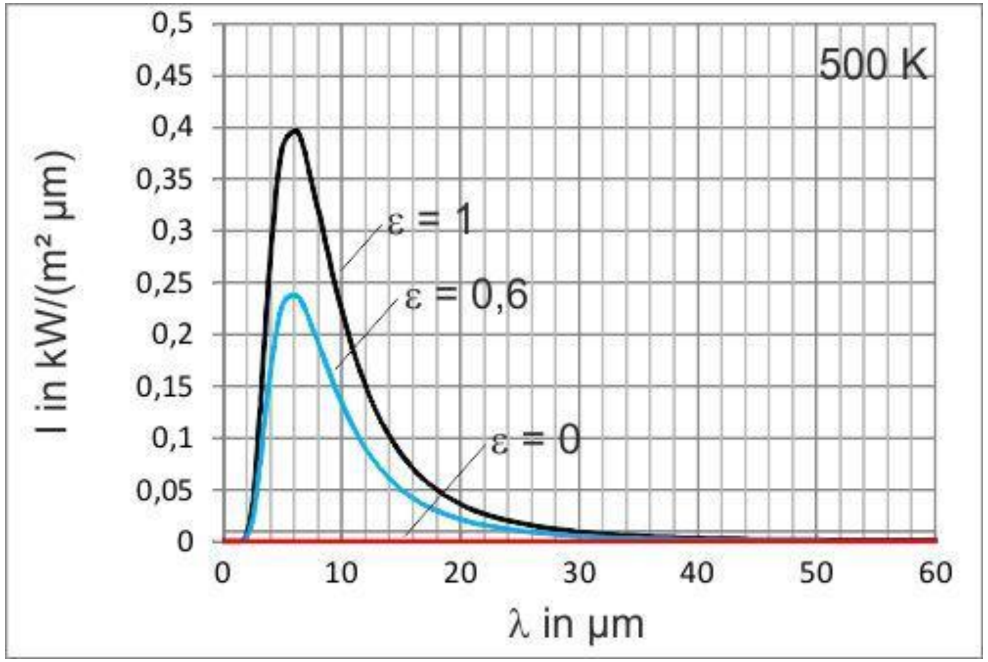
Radiative equilibrium matter/radiation

If Q_{abs} = constant < 1, the matter radiated spectrum will be $Q_{abs} B_\nu(T)$, a «scaled» version of $B_\nu(T)$. This is called a «grey body»: matter has the same temperature of the blackbody radiation incident on it, although it emits radiation, at each wavelength, in a constant ratio less than unity to that emitted by a black body at the same temperature

Matter and radiation are, in this case, in mutual thermal and radiative equilibrium with each other, having the same temperature and being the incident power absorbed by the matter equal to the power radiated . The grey body can acquire the same temperature of the incident BB radiation just because, even if it absorbs only *some* of the incident radiation, it also emits only *some* of the absorbed radiation.

But the thermal radiation emitted by the grey body is not a real Planckian:





Here ε is the emissivity j_ν / j_ν^{BB} (that we called Q_{em})

Problem 6. In open, inhomogeneous systems, in rarefied matter partially permeable to radiation (i.e., optically thin medium), the absence of a mutual equilibrium matter/radiation allows the formation of spectra different from the Planck distribution. Assuming the matter in thermal equilibrium, consider the transfer equation in presence of scattering. Write it in the two cases:

1) Absorption dominates over scattering;
2) Scattering dominater over absorption.

In case 2), what happens if the radiation field is isotropic?

Problem 7. Compare the emission spectrum of a grey body at temperature T with the spectrum of a blackbody at the same temperature.

1) Is the brightness peak of the two spectra occurring at the same frequency? Why?

2) How do you expect the photon occupation number to be for the grey body radiation with respect to that of the blackbody radiation with the same temperature? And the chemical potential?

3) Is it correct to define the grey body radiation at temperature T as a gas of photons in thermodynamic equilibrium with itself?

Problem 8. Consider a body in LTE, emitting thermal radiation. Suppose its absorption efficiency Q_{abs} is a function of the frequency, $f(\nu)$. Is it correct to define the thermal radiation as radiation in thermodynamic equilibrium with itself? If not, what would be necessary to make it become a Planckian distribution?

Problem 9. Consider the setting of the Kirchhoff's ideal experiment. Suppose the walls of the enclosure are opaque (no transmission through the walls), but the material of the walls is partially reflecting light (coherent diffusion), so that the absorption efficiency of the walls is $Q_{abs}<1$ while $\alpha_{scattering} \neq 0$. Piercing the walls without perturbing the equilibrium, we know that we'll detect Blackbody radiation, which is radiation emitted by a perfect absorber/emitter (i.e., the effective Q_{abs} of the system is $= 1$). Why doesn't the scattering inside the box prevent the effective Q_{abs} to be equal to unity?