4. Blackbody Radiation, Boltzmann Statistics, Temperature, and Thermodynamic Equilibrium

Blackbody radiation, temperature, and thermodynamic equilibrium give a tightly coupled description of systems (atmospheres, volumes, surfaces) that obey Boltzmann statistics at the macroscopic level. They are important because of the compact descriptions of systems that they give when Boltzmann statistics apply, either approximately or nearly exactly. Fortunately, this is most of the time in the Earth's stratosphere and troposphere, and in other planetary atmospheres as long as the density is sufficient that collisions among atmospheric molecules, rather than photochemical and photophysical properties, determine the energy populations of the ensemble of molecules. The description is compact because the definition of temperature implies thermodynamic equilibrium, Boltzmann statistics, and blackbody radiation as a limiting case of the emission of radiation.

4.1 Thermodynamic Equilibrium

The existence of thermodynamic equilibrium in a closed volume of gas (well approximated by a small atmospheric air parcel, of cm-scale size or larger at the tropopause or below, based on collisional mean free paths of air molecules) means that the total energy of the gas volume and its partitioning among different energy levels (*i.e.*, the internal rotational, vibrational, and electronic levels and the translational energy) do not change macroscopically over time. The microscopic state remains in constant flux at equilibrium due to the changes in internal and translational energies caused by collisions and the absorption and emission of radiation; these changes average to zero macroscopically.

4.2 Boltzmann statistics

Consider a simplified set of energy states an atom or molecule may occupy (**Figure 4.1**). There are a number of discrete energy states and, above the *dissociation limit*, where the molecule is no longer chemically bound, a continuum described by the density of states $\rho(E)$. At thermal equilibrium, the *Boltzmann factor*, which gives the relative population for a given bound state, *i*, with discrete energy E_i, is $e^{-E_i/kT}$, where *k* is Boltzmann's constant and *T* is the temperature.

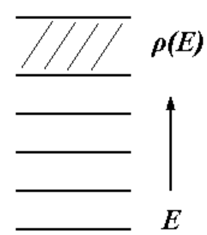

Figure 4.1. A simplified energy level diagram for an atom or molecule, including discrete bound states and a density function of continuum states.

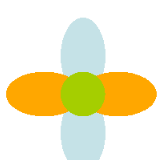

Figure 4.2. Triply degenerate *p*-orbitals of an atom.

The concept of *degeneracy* of states is also required for the Boltzmann description. This is nothing more than the realization that there are, in many or most cases, more than one distinct quantum state at a given energy. As an example, in the familiar case of a set of *p*-orbitals of an atom (shown schematically in **Figure 4.2**), there are three distinct states, where the lobes of the orbitals (each of which can house two electrons) are oriented along either the *x*- *y*- or *z*-axis. These orbitals are degenerate in energy unless their spatial symmetry is broken by an external interaction. In the soon-to-be-familiar case of the rotational states of a diatomic molecule, a state with rotational angular momentum J has a degeneracy of $2J+1$. This degeneracy may be *broken* by an electric field $\vec{E}$ or magnetic field $\vec{m}$, if the molecule has either an electric or magnetic dipole moment, to separate the states in energy. The degeneracy g_i = the number of energy levels with energy E_i. **Figure 4.3** shows an example appropriate to rotational levels of a linear molecule (*cf.* **Chapter 6.2**).

For statistical mechanics purposes, degeneracy thus simply means having more than one state at a particular energy. Boltzmann statistics may then be described starting from the Boltzmann factors that give relative populations. For the discrete states, the population in each state

$$P_i \propto e^{-E_i/kT}. \tag{4.1}$$

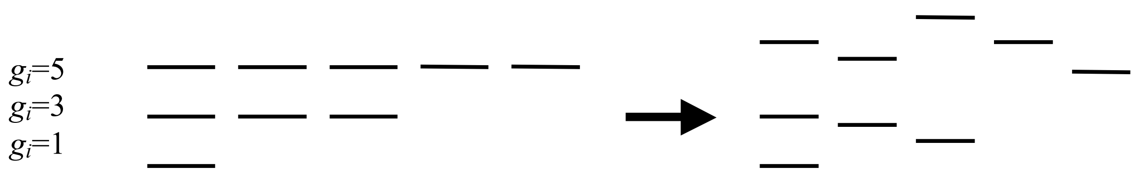

Figure 4.3. Degenerate energy levels appropriate to rotational levels of a linear molecule are shown on the left. The right side demonstrates how the degeneracy may be broken, e.g., by a magnetic field $\vec{m}$ or an electric field $\vec{E}$, if the molecule has a magnetic or an electric dipole moment, respectively.

The population at each energy

$$P_{E_i} \propto g_i e^{-E_i/kT}. \tag{4.2}$$

The *partition function* Q describes how relative population numbers are apportioned among the different energies and states: $Q \equiv \sum_i g_i e^{-E_i/kT}$. (4.3)

The extension to include continuum states is straightforward:

$$Q \equiv \sum_{i=1}^{b} g_i e^{-E_i/kT} + \int_b^{\infty} \rho(E) e^{-E/kT} dE. \tag{4.4}$$

The continuum term will be omitted from further discussions. It is not normally needed in atmospheric spectroscopy since the dissociation energies are so high that continuum states do not normally contribute to the populations of planetary atmospheres in near-equilibrium conditions. It can readily be reintroduced as needed, substituting the sum over states with the integral over density of states as in **Eq. (4.4)**. The partition function provides the normalization factor so that fractional populations for states are given as:

$$P_i = e^{-E_i/kT}/Q. \tag{4.5}$$

The fractional population at energy E_i,

$$P_{E_i} = g_i e^{-E_i/kT}/Q. \tag{4.6}$$

The normalization by Q also makes the arbitrary choice of the zero of energy (the origin of the energy levels) cancel out of the population statistics (problem 4.1).

Some definitions may now be stated more firmly:

- A system at equilibrium is one where the populations of energy levels are described by Boltzmann statistics.
- A system at equilibrium may be described by a temperature and, conversely;
- Temperature is a characteristic of an equilibrium system. A system that is not at equilibrium does not have a defined temperature. (In the early days of laser development, the achievement of a population inversion, necessary for lasing or masing, has been described as achieving a *negative temperature*, *i.e.*, $e^{-E_{upper}/kT} > e^{-E_{lower}/kT} \Rightarrow T < 0$).
- At equilibrium, the radiation is in equilibrium with the molecules, at the same temperature. Their energy distributions are described by the blackbody radiation law, which will be introduced in the next section.

Local thermodynamic equilibrium

The expression *local thermodynamic equilibrium* (LTE) is frequently encountered, particularly in astrophysics and atmospheric science. This is simply a way of expressing that local behavior (say at a certain altitude in the atmosphere) is reasonably well described as being in equilibrium and characterized by a temperature, whereas on larger scales, where the atmospheric structure varies, this cannot be the case, since the temperature varies. As a very rough rule, LTE in a region of an atmosphere is established when there are ≥ 10 collisions per photochemical or reaction event. In the Earth's atmosphere, non-LTE conditions are normally encountered in the mesosphere and above, with mesospheric CO_2 as a common example.

An atmosphere may be stable even though it is not overall in equilibrium, depending on the boundary conditions of gravity and heating. Most atmospheres are not completely in equilibrium (no planetary atmospheres are): Since the Earth's troposphere is heated from the bottom, and warmer air is more buoyant, there is a natural mixing as a counter effect to the thermodynamic temperature lapse (*tropos* is Greek for "to turn"). The stratosphere, on the other hand, is heated internally, mainly through absorption of ultraviolet radiation by ozone. This heating increases with height relative to atmospheric density. The stratosphere is more *stratified*, and stable.

Situations where a system is described by more than one temperature are frequently encountered. For example, in an astrophysical plasma, one may hear of a "radiation temperature" and a different "kinetic temperature." In this case the separate phases (radiation and matter) are reasonably well described by temperatures, but are not strongly enough coupled together through absorption and emission to establish equilibrium. Analogously, in laboratory spectroscopy, one frequently hears of separate rotational and vibrational temperatures produced by certain sample preparation techniques (*e.g.*, supersonic expansions in molecular beams).

4.3 Blackbody radiation

A blackbody is an idealized object that absorbs and emits radiation at all wavelengths with 100% efficiency. Although a blackbody is an ideal situation, it is a fundamentally important limit for emission and absorption spectroscopy, as will be described in **Chapter 5**. Someone who has encountered a buffalo or a moose on a road at night may perceive it as a pretty good blackbody! A blackbody is completely characterized by a temperature *T* and as such obeys several convenient laws as described below. Blackbody emission is Lambertian.

Relation of intensity with wavelength and temperature (Planck's law)
The Planck's law blackbody flux density for emission from a surface *per wavenumber* is:

$$R_\sigma = \frac{2\pi hc^2\sigma^3}{e^{hc\sigma/kT}-1}, (e.g., \text{ in W m}^{-1} \text{ or erg s}^{-1} \text{ cm}^{-1}), \tag{4.7}$$

where σ is the wavenumber, (*e.g.* m^{-1} or cm^{-1}), *h* is the Planck constant, *c* the speed of light, and *k* the Boltzmann constant. Including the increment in wavenumber $d\sigma$ gives $R_\sigma d\sigma$, flux density in power per unit area,

$$R_\sigma d\sigma = \frac{2\pi hc^2\sigma^3 d\sigma}{e^{hc\sigma/kT}-1}. \tag{4.8}$$

The blackbody *radiation density*, defined as the radiation density inside a *hohlraum*, a cavity whose walls are at a constant temperature and in thermodynamic equilibrium with the inside, is

$$\rho(\sigma)\,d\sigma = \frac{8\pi hc\sigma^3 d\sigma}{e^{hc\sigma/kT}-1}. \tag{4.9}$$

Radiation constants
The first radiation constant $c_1 \equiv 2\pi hc^2 =$ 3.74177×10^{-16} W m^2. The second radiation constant $c_2 \equiv hc/k = 1.43878\times10^{-2}$ m K. The emitted flux density is thus:

$$R_\sigma d\sigma = \frac{c_1\sigma^3 d\sigma}{e^{c_2\sigma/T}-1}. \tag{4.10}$$

Often, excitation levels are given in K rather than in wavenumbers, for convenience in relating atomic and molecular physics to a particular temperature regime. c_2 provides the relationship between them.

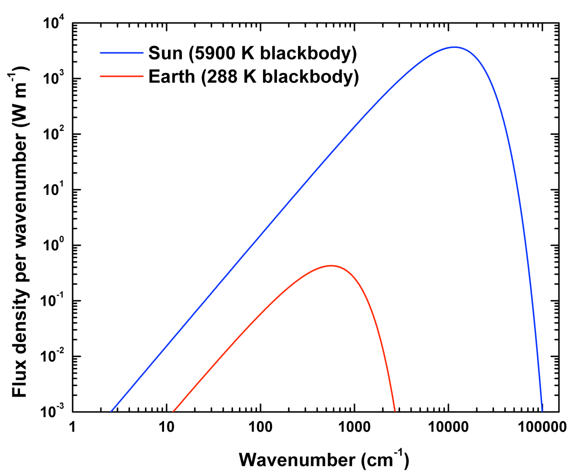

Figure 4.4 Blackbody emission per unit area is greater at every wavenumber when the temperature is higher. The Sun and Earth are approximated here as blackbodies.

In photons ($E = h\nu = hc\sigma$),

$$R_n(\sigma)d\sigma = \frac{2\pi c\sigma^2 d\sigma}{e^{c_2\sigma/T} - 1} = \frac{1.88365\times 10^{11}\sigma^2 d\sigma}{e^{c_2\sigma/T} - 1}. \quad (4.11)$$

The blackbody emission per unit of emitting area increases with increasing temperature at all wavenumbers (**Figure 4.4**). It is also greater per unit solid angle of observed area. Problem 4.2 determines the flux density per unit solid angle. In spectroscopy of the Earth's atmosphere, the balance of radiation from the Earth and the Sun in the infrared is due to the much larger angular size of the Earth (Problem 4.3 and **Figure 5.6**).

Rayleigh-Jeans limit

For $h\nu \ll kT (hc\sigma \ll kT)$, R_σ is approximately linear with temperature:

$$\frac{2\pi hc^2\sigma^3 d\sigma}{e^{hc\sigma/kT} - 1} \simeq 2\pi kTc\sigma^2 d\sigma. \quad (4.12)$$

This is in common use in radiofrequency and microwave work, especially in radio astronomy. This law was first discovered empirically, and then led to the predicted *ultraviolet catastrophe*. That is, emission versus wavenumber and total emission become infinite! It was known to be wrong but it was classically required: Quantum theory was required for the derivation of Planck's law (Davidson, Chapter 6).

Antenna temperature, noise temperature, system temperature

Radio astronomers and aeronomers measuring at frequencies where the Rayleigh-Jeans limit applies give power sources as temperatures. This includes target signals as well as aspects of the instrumentation (detector noise and other noise sources) and the entire instrument (the *system*) in this way. This simply means that each contribution is equal to that which would arise from a blackbody at that temperature in signal power or noise power. This is discussed in more detail under noise sources in **Section x.y**.

Emissivity, reflection coefficient, Kirchoff's law

A blackbody is the most a surface at temperature T can emit. It can emit less:
Emissivity: $\varepsilon \le 1$. The emissivity ε_λ of a medium (gas, liquid, or solid) at wavelength λ equals its absorptivity A_λ. Thus, for a blackbody, $\varepsilon_\lambda = A_\lambda = 1$. For a non-blackbody, $\varepsilon_\lambda = A_\lambda < 1$.The reflectivity R_λ is 0 for a blackbody: $\varepsilon_\lambda + R_\lambda = 1$. In general, blackbody or not, the emission and reflection are exactly balanced:
Reflection coefficient (reflectivity): $R \le 1$.
Kirchoff's law: $\varepsilon + R = 1$ for *opaque* surfaces (the extension to include transmission is straightforward).

Relation between flux density and temperature (Stefan-Boltzmann constant)

The total flux density F of a blackbody can be calculated by integrating a blackbody over wavenumber:

$$F = \int_0^\infty R_\sigma d\sigma = 5.67037\times10^{-5} \text{ erg cm}^{-2} \text{ s}^{-1} \text{ }^o\text{K}^{-4} = 5.67037\times10^{-8} \text{ W m}^{-2} \text{ }^o\text{K}^{-4}.$$

Relation between maximum intensity and temperature (Wien's law)

The wavelength of maximum intensity of blackbody radiation is proportional to temperature as illustrated in **Figure 4.4**. The maximum

- power per wavenumber occurs at σ_{max} (cm^{-1}) = 1.96101T (^{o}K)
- number of photons per wavenumber occurs at σ (cm^{-1}) = 1.10763T (^{o}K)
- power per wavelength occurs at λ (μm) = 2897.77 / T (^{o}K)
- number of photons per wavelength occurs at λ (μm) = 3669.70 / T (^{o}K)

References

Davidson, N.R., "Statistical Mechanics," McGraw-Hill, New York, 1962. A good source for further information especially on statistical aspects of the development of the concepts of statistical mechanics.

Penner, S.S., "Quantitative Molecular Spectroscopy and Gas Emissivities," Addison-Wesley, Reading, MA, ISBN: 0201057603, 1959. Great detail on blackbody radiation.

Problems (assigned February 11, due February 20)

4.1 Demonstrate that the determination of fractional populations of states and energy levels using Boltzmann factors and the partition function is independent of the choice of the zero of energy (the origin of the energy levels).

4.2 Determine the blackbody radiance (emitted flux density per steradian) from Equation 4.10 by invoking Lambertian emission and integrating over solid angle.

4.3 The Sun may be approximated by a blackbody at 5900 ^{o}K. The average temperature of the Earth is near 288 ^{o}K. For these temperatures and for a satellite orbiting the Earth at 800 km, on the sunlit part of the orbit, at what wavenumber does the radiation received from the Earth equal that received from the Sun?

4.4 Calculate the fraction of radiation emitted at visible wavelengths for a typical incandescent light bulb (filament T = 3000 ^{o}K). What is the wavelength of maximum emission?