Local Thermodynamic Equilibrium

A key atmospheric concept is *Local Thermodynamic Equilibrium.* If the atmosphere was not in LTE we couldn't define temperature. Here we describe what this means.

Local thermodynamic equilibrium means that *over time scales of interest* fluctuations in the Boltzmann distribution between energetic modes are so fast that effectively all modes are in equilibrium with each other. This sounds very abstract but it is critically important because it means that we can describe a volume of air as having a temperature and pressure.

With respect to the atmosphere, the energy associated with a molecule has two major components: the kinetic energy associated with translational motions (molecular movement in space), and the kinetic energy associated with molecular scale energy transitions

$$e_{Total} = e_{trans} + e_{mol}$$

The molecular scale energy can in turn be broken up into rotational, vibrational, vibrational-rotational and electronic transition components (plus a few others that we won't concern ourselves with here)

$$e_{total} = e_{trans} + e_{rot} + e_{vib} + e_{elec} + \ldots$$

Each of these components, as we discussed, has several, modes or degrees of freedom. Translational energy has three degrees of freedom: one each in the x, y, and z directions. For internal energy, CO_2 for example has two rotational degrees of freedom, three distinct vibrational degrees of freedom, and many, many vibrational-rotational degrees of freedom.

Translational energy is what we sense as temperature. A classical treatment works fine here. Each degree of translational freedom has kinetic energy

$$e_{trans\,x} = \frac{1}{2}kT$$

for a total in the x, y, and z direction (3 DOFs)

$$x_{trans} = \frac{3}{2}kT$$

This energy is what we interpret as "temperature" in daily life (more on this later). It is the kinetic energy of the molecules that causes the pressure on our skin that we interpret as heat.

Molecular energy is more complicated. Every DOF is associated with an energy transition. At an equilibrium we find that, averaged over a large number of molecules, the probability that we will find a molecule with a particular energy level is determined by what is known as the Boltzmann distribution. Ignoring that some modes are degenerate (different physically but with the same energy), consider a hypothetical molecule with two energy levels 0 and 1 (0 being the ground). Then the relative population of state 1 to state 0 is given by

$$\frac{n_1}{n_0} = \exp\left(-h\nu/kT\right)$$

i.e. there's exponentially fewer in a particular energy state, the higher the energy level. In fact we see this exponential expression as part of the Planck radiation equation

$$B_\nu = \frac{2h\nu^3}{c^2\left(e^{h\nu/kT} - 1\right)}$$

In fact, maintenance of this distribution is what creates the Planck blackbody radiation. Notice that this radiation depends on temperature also, but in a way that depends not at all on the translational motions of the molecules but rather *only the energy transitions within the molecules themselves*. So really, we have two completely different temperatures

Thermal Temperature $\frac{3}{2}kT_{therm}$

Planck Temperature $B_\nu(T_{Planck})$

Local Thermodynamic Equilibrium, the precondition for Kirchoff's Law, and what applies to the bottom 60-70 km of our atmosphere, requires that

$$T_{therm} \equiv T_{Planck}$$

How does this happen?
   Imagine the following sequence of events

1. A molecule maintains a Boltzmann distribution that is a function of its radiating temperature T_{Planck}

2. The molecule is bombarded by electromagnetic radiation that, if it is at frequencies corresponding to molecular modes, disturbs the Boltzmann distribution, raising molecular energies over all to a higher state.

3. Two things can happen here. If left to themselves, the molecule will reestablish a Boltzmann distribution by releasing photons (energy). This is what causes the Northern Lights. However, if the pressure of the gas is high enough, the molecules collide before this release of energy can happen. Instead, through collisions, the molecular energy gets passed between molecules and gets turned into kinetic energy.

4. Through continual absorption of radiative energy, and redistribution as kinetic energy, an equilibrium is maintained between e_{trans} and e_{mol} such that

$$T_{therm} \equiv T_{Planck}$$

   For atmospheric pressure above 0.05 mb (i.e. 99.5 % of the atmosphere) this condition applies.

Maintenance of LTE is usually glossed over in introductory texts because it applies to most of the atmosphere. However, understanding why it occurs is integral to understanding why our planet is livable, i.e. how it is that radiative energy is converted to the thermal energy that keeps our planet warm. The concept of temperature really is conditional on an assumption that a system is in LTE.

Kirchoffs Law

Under conditions of Local Thermodynamic Equilibrium, we often hear that Kirchoff's Law applies, which states that the emissivity of a layer is equivalent to the absorptivity

$$\varepsilon_\lambda = \alpha_\lambda$$

The premise here is that if an object has a temperature T and an absorptivity $\alpha_\lambda < 1$ then it is not a blackbody. Something may have an absorptivity less than unity at a particular wavelength if it is transparent or shiny. A blackbody absorbs all radiation incident upon it at a particular wavelength, hence its emissivity is unity. To see why Kirchoff's law holds consider that at LTE there must be equilibrium between total absorption and emission. Otherwise temperature would be changing. Thus absorption equals emission and

$$\int_0^\infty \alpha_\lambda B_\lambda d\lambda = \int_0^\infty \varepsilon_\lambda B_\lambda d\lambda$$

implying that

$$\varepsilon_\lambda = \alpha_\lambda$$

Note that an object can still absorb more radiation than it emits *at a particular wavelength* - if, for example, the radiation it absorbs is coming from another object with a higher temperature.

For example, consider object a and object b with $T_b \ll T_a$. Object a radiates energy

$$F_a = \sigma T_a^4$$

Object b absorbs a fraction of energy from a at a particular wavelength according to its absorptivity:

$$F_{b\lambda}(absorbed) = \alpha_\lambda \sigma T_a^4$$

It reemits the energy with emissivity

$$\varepsilon_\lambda = \alpha_\lambda$$

but at temperature T_b. Thus

$$F_{b\lambda}(emitted) = \varepsilon_\lambda \sigma T_b^4$$

Notice that $F_{b\lambda}(emitted) \ll F_{b\lambda}(absorbed)$, even though the emissity and absorptivity are the same, because $T_b \ll T_a$.