Rate Equations and Detailed Balance

Initial question: Last time we mentioned astrophysical masers. Why can they exist spontaneously? Could there be astrophysical lasers, i.e., ones that emit in the optical?

Blackbodies arise if the optical depth is "big enough". What does that mean? It means that all processes are in equilibrium with their inverses, so there is no net change in the chemical composition, ionization fraction, or whatever. If you can establish that this is the case in a particular situation, you are justified in assuming a blackbody. Even if it isn't exactly a blackbody, you can show in many cases (e.g., in stellar interiors) that in a local region (say, within one mean free path) your matter is close to equilibrium, so you assume LTE: Local Thermodynamic Equilibrium. This simplifies things greatly, so if you can show that LTE applies you can heave a sigh of relief.

Ask class: can they think of astronomical situations in which LTE is a bad approximation? The interstellar medium is a good example; it's optically thin, and there are all sorts of nonequilibrium processes. In that case you can't assume equilibrium and must instead go to the fundamental rate equations.

A side note: in countless situations involving radiative processes and other astrophysics it is a good idea to determine if your system is in equilibrium in one way or another. If it is, you are allowed drastic simplifications. For example, **Ask class:** is the Sun in equilibrium? We'd have to say what that means. The free-fall time for the Sun would be about an hour if nothing stopped it, but the Sun has been shining away for billions of years, so it's in dynamic equilibrium. Look for this kind of equilibrium, but always check first, otherwise you could mislead yourself a lot!

Okay, back to rate equations. In principle you would think that you would have multiple unrelated rates for a given process. For example, consider a two-level atom: ground state (level 1) and excited state (level 2). There's an absorption rate ($1 \rightarrow 2$), a spontaneous emission rate ($2 \rightarrow 1$), and a stimulated emission rate (also $2 \rightarrow 1$). We know from Kirchoff's law ($j_\nu = \alpha_\nu B_\nu$) that for a thermal emitter at least there is some relation between emission and absorption, so we might suspect there is a microscopic relation between the two. In fact, Einstein (1916) showed that all three rates are related to each other *whether or not the system is in thermal equilibrium*! This is called the *principle of detailed balance*, and it simplifies the analysis of rates considerably.

Let's follow Einstein's treatment of a two-level atom. Let A_{21}, the "Einstein A coefficient", be the rate of spontaneous emission. This is the transition probability per unit time that an atom currently in level 2 will go to level 1.

Now let's assume that the atom is in the midst of a radiation field with a mean intensity at frequency ν of $J_\nu = (1/4\pi)\int I_\nu\, d\Omega$. Note that the difference in energies between level 2 and level 1 can't be defined with infinite precision, because of the uncertainty principle. Let us therefore be careful and define a *line profile* $\phi(\nu)$ that is sharply peaked at the line center ν_0 and is normalized so that

$$\int_0^\infty \phi(\nu)\, d\nu = 1\ . \tag{1}$$

We can define an average intensity over this profile, $\bar{J} = \int_0^\infty J_\nu \phi(\nu)\, d\nu$. Note that if J_ν varies slowly over the line profile (which it almost always does), this practically reduces to J_{ν_0}, but it's nice to be careful.

Ask class: what effects can the external radiation field produce on the atom? Absorption or stimulated emission. Now, we'd like to assume that the absorption rate and stimulated emission rate are both proportional to $\bar{J}$, i.e., they are linearly proportional to intensity. As always, though, we want to be sure we know when this simplifying assumption can become invalid. This is a tough one, though: **Ask class:** when might this be incorrect? The linear relation could break down if the radiation is self-interacting, which might happen at extremely high intensities or with high photon energies (when processes such as pair production enter in). In almost all applications this is insignificant, but if you're analyzing a very high energy environment (e.g., gamma-ray bursts) you should be cautious.

Anyway, let's apply that assumption. Then we have a transition rate of $B_{12}\bar{J}$ for absorption and $B_{21}\bar{J}$ for stimulated emission, where B_{12} and B_{21} are the Einstein B coefficients. How are the three coefficients related to each other? We'll start by analyzing the situation in thermodynamic equilibrium. For this analysis we assume that the upper level has a statistical weight of g_2 and the lower level has a statistical weight of g_1. We also assume that in equilibrium there are n_2 atoms in level 2 and n_1 in level 1.

Ask class: what relation does equilibrium imply? It implies that the rate from level 1 to 2 equals the rate from level 2 to 1, or

$$n_1 B_{12}\bar{J} = n_2 A_{21} + n_2 B_{21}\bar{J}\ . \tag{2}$$

Therefore,

$$\bar{J} = \frac{A_{21}/B_{21}}{(n_1/n_2)(B_{12}/B_{21}) - 1}\ . \tag{3}$$

In equilibrium, the level populations n_1 and n_2 are given by the Boltzmann distribution, which says that the number is proportional to the statistical weight times $\exp(-E/kT)$, where E is the energy of the level. We're taking a ratio, so the zero point of the energy doesn't matter and therefore

$$\bar{J} = \frac{A_{21}/B_{21}}{(g_1 B_{12}/g_2 B_{21})\exp(h\nu_0/kT) - 1}\ . \tag{4}$$

Here $h\nu_0$ is the energy difference between the levels, with level 2 assumed to have higher energy than level 1. We also know, however, that in thermodynamic equilibrium $J_\nu = B_\nu$, the Planck function. Since the Planck function varies slowly over a sharp line profile, $\bar{J} = B_\nu$. This expression must hold for all temperatures and for all frequencies ν_0. The only way this can happen is if the *Einstein relations* hold:

$$\begin{aligned} g_1 B_{12} &= g_2 B_{21} \\ A_{21} &= (2h\nu^3/c^2) B_{21} \ . \end{aligned} \tag{5}$$

Now let's sit back and meditate on what we've just shown. You might think that we have only shown that certain relations hold in thermal equilibrium. But actually this is much more general. Consider: none of the coefficients A_{21}, B_{12}, and B_{21} can depend on the external radiation field. A_{21} is a *spontaneous* emission coefficient, so it doesn't interact with the external field at all. Also, since we have assumed that the rates of absorption and stimulated emission are *linearly* proportional to the mean intensity, the B coefficients are also independent of any properties of the radiation field. Think of this another way: the B coefficients only depend on a narrow range of frequencies near ν_0, so they don't "know" about the full spectrum. Thus, it can't be relevant whether the full spectrum is a blackbody or not, or even what the intensity is. As a result, the Einstein relations always hold given our assumption that the mean intensity enters linearly.

Let's develop our intuition a bit more with a couple of problems from the book. **Ask class:** what result do we expect if stimulated emission is ignored? This isn't obvious, but it's good to take a guess anyway so we can learn more after doing the problem.

Again using the trick of thinking first about thermal equilibrium, we now have

$$n_1 B_{12} \bar{J} = n_2 A_{21} \ . \tag{6}$$

Using the Boltzmann distribution this implies

$$\bar{J} = (g_2 A_{21}/g_1 B_{12}) \exp(-h\nu_0/kT) \ . \tag{7}$$

Ask class: can this equal the Planck function with A_{21} and B_{12} independent of temperature? Nope, the functional form is wrong. However, we do find that if $A_{21}/B_{12} = (2h\nu_0^3/c^2)(g_1/g_2)$ then $\bar{J}$ equals the Planck function in the Wien limit $h\nu_0 \gg kT$. This says that stimulated emission is negligible in the Wien limit. **Ask class:** why is this true? It's because the Wien limit is where the number of photons in the radiation field drops off exponentially. Since stimulated emission is proportional to the number of photons whereas spontaneous emission is independent of the number of photons, there will come a point when stimulated emission can be ignored.

Now another example. Suppose that the atom interacts with a neutrino field instead of a photon field. As we'll discuss more next time, a neutrino is a fermion (a photon is a boson), so that two or more neutrinos cannot occupy the same state. As a result, instead of stimulated emission you'd have suppressed emission:

$$n_1 B_{12} \bar{J} = n_2 A_{21} - n_2 B_{21} \bar{J} \ . \tag{8}$$

In addition, in thermal equilibrium the mean intensity is

$$J_\nu = \frac{2h\nu^3/c^2}{\exp(h\nu/kT) + 1} \ . \tag{9}$$

Ask class: if we carry through the same analysis as before, what would they guess would be the "neutrino Einstein relations"? As you can verify directly, you get exactly the same expressions as we had before! This is a dramatic indication that the Einstein relations are properties of the atomic physics and have nothing whatsoever to do with the properties of an external radiation field! Essentially, bringing in the field is just a convenient way to get the answer, but it isn't necessary.

We can express the emission and absorption coefficients using the Einstein coefficients. Let's assume that the line profile for emission is the same as it is for absorption (a very good assumption most of the time). Then, as derived in the book, the emission coefficient is

$$j_\nu = (h\nu_0/4\pi) n_2 A_{21} \phi(\nu) \tag{10}$$

and the absorption coefficient is

$$\alpha_\nu = (h\nu/4\pi)\phi(\nu)(n_1 B_{12} - n_2 B_{21}) \ . \tag{11}$$

Note that again stimulated emission is acting like a negative absorption. For the record (and again from the book, equation 1.6), the transfer equation then becomes

$$dI_\nu/ds = -(h\nu/4\pi)(n_1 B_{12} - n_2 B_{21})\phi(\nu) I_\nu + (h\nu/4\pi) n_2 A_{21} \phi(\nu) \tag{12}$$

and the source function is

$$\begin{aligned} S_\nu &= n_2 A_{21}/(n_1 B_{12} - n_2 B_{21}) \\ &= (2h\nu^3/c^2)/\left(\frac{g_2 n_1}{g_1 n_2} - 1\right)^{-1} \ . \end{aligned} \tag{13}$$

Note that the A coefficient has different units from the B coefficients (the latter, multiplied by I_ν, give the units of A_{21}). Also, note that it is pointless to memorize equations such as this. You can get an idea of what the answer should be by asking yourself how the intensity should change. Clearly, the intensity will increase if there is spontaneous emission or stimulated emission, and decrease if there is absorption. Also, remember that absorption and stimulated emission are proportional to I_ν whereas spontaneous emission isn't. That should allow you to piece together most of the important parts.

If the matter is in thermal equilibrium with itself, but not necessarily with the radiation, we have local thermodynamic equilibrium and $n_1/n_2 = (g_1/g_2)\exp(h\nu/kT)$. You can verify that this makes $S_\nu = B_\nu$. In all other cases (nonthermal emission), this equality does not hold. A particularly cool way in which matter can be out of thermal equilibrium is in a laser or maser (the same phenomena but different wavelengths; however, masers are found in space whereas lasers tend to be laboratory creations). Let's divert with these a bit.

Suppose for simplicity that $g_1 = g_2$ (equal multiplicity of the two states). Then $B_{12} = B_{21}$. **Ask class:** if $n_1 > n_2$, which dominates, absorption or stimulated emission? Absorption. This is the normal case, because $E_2 > E_1$ so in thermal equilibrium (or even most forms of non-thermal distributions) the lower-energy state is more populated. **Ask class:** but what if $n_2 > n_1$? Then the intensity *increases* exponentially along the path of the beam. Moreover, although it isn't clear from our discussion here, bosons (e.g., photons) like to occupy the same quantum state, so the direction and phase of the emitted photon is the same as that of the original photon. This means tremendous intensity!

Just for fun, let's think about what conditions might allow a laser/maser. **Ask class:** what are the requirements? We need an inverted population, which has higher energy than the normal population, meaning we need some supply of energy. Another, trickier, requirement is that the upper state must persist for a while (otherwise spontaneous emission will reduce the number of atoms in the upper state). In practice this often means that the level structure has to be complicated: excitation can occur to another state, say state 3, which decays to state 2. State 2 is then metastable, meaning it has a long time before it will decay.

In the lab it takes lots of special preparation to get all this to work, mainly because the number densities (of gas, liquid, or solid) are high enough that thermal equilibrium (specifically a normal population) can be established rapidly. In space, the number densities are much less and therefore it is a lot easier for inverted populations to exist. The result is that masers are common in astronomy: around very young stars, around old stars, in the centers of galaxies, and so on. The tiny size of masing regions, plus their high intensity and extreme frequency coherence, makes them remarkably good probes of astrophysical conditions.