ASTR 4017/8007: Diffuse Matter in the Universe

Class 2 Notes: Statistical mechanics

In the last class we developed a basic theory of particle-particle collisions. In this class we will make use of that microphysical theory to develop a macroscopic theory for the behavior of the ISM, based in statistical mechanics. We will first try to understand under what conditions we can think of the ISM as a gas with the same sort of particle velocity distribution we're used to at higher density, i.e., that the gas has bulk velocity and that the distribution of individual particle velocities is simply the bulk velocity added to a Maxwellian distribution. We will then use the results of this investigation to derive two general and powerful results regarding reactions in the ISM (and elsewhere): the law of mass action and the principle of detailed balance.

I. Fluid behavior

The first topic to discuss today will be when we can consider a collection of particles to be a fluid, and under what circumstances we can describe it meaningfully as having a single temperature. To answer this question, we first have to recall what it means for something to be a fluid. If we study the air in this room and we focus on a volume so small that it contains only 2 molecules, then clearly a fluid description is meaningless. If we focus on a larger volume, eventually we're looking at something where it is meaningful to assign a single velocity, density, etc. Similarly, it makes no sense to talk about the temperature of two atoms. We need to have enough to fill out a distribution. Our goal is to figure out the scale that separates the regime where we need to think about a collection of individual particles from the regime where we can talk in terms of statistical and collective properties.

A. Fluid behavior: neutral particles

Let's start with the question of over what scales we can consider something a fluid. The requirement here is that particle velocities be randomised so that they are equal to the bulk, macroscopic velocity of the fluid, plus a random component. When averaged over many particles, the random components will average out. Such a random, isotropic distribution will be established only on length scales where particles collide often enough to isotropise their motions.

Let's start with the simplest case: a set of identical neutral particles, say hydrogen atoms. Since any scattering between two such particles is enough to redirect their motion in an arbitrary direction, I can consider things a fluid on scales significantly larger than the particle mean free path. For neutral particles undergoing hard-sphere scattering, this length is

$$\lambda_{\mathrm{mfp}} = \frac{1}{n\sigma} = 55 \left(\frac{r}{1\ \text{Å}}\right)^{-2} \left(\frac{n}{1\ \mathrm{cm}^{-3}}\right)^{-1}\ \mathrm{AU}, \tag{1}$$

where r is the particle radius.

For a population containing particles of very disparate masses the question is more complicated, because a massive particle will not change its momentum much per encounter with much less massive particles. Instead, it will take many encounters to change the massive particle's direction significantly.

B. Fluid behavior: charged particles

Another case that is more complicated is the case of collisions between ionised particles, because in that case, as we have seen, the cross section is not a well-defined quantity due to the long range Coulomb interaction. Instead, we must ask about how long it takes the particle's momentum to change significantly as a result of all those Coulomb interactions.

Consider a particle of charge $Z_1 e$ moving through a field of particles of charge $Z_2 e$. We have seen that the change in particle 1's transverse momentum due to an encounter at impact parameter b and velocity v is

$$\Delta p_\perp = 2\frac{Z_1 Z_2 e^2}{b v_1}. \tag{2}$$

On average the momentum change due to the many particles in the field will sum to zero, but the RMS change will not be zero – the particle's transverse momentum will undergo a random walk. We can compute the rate at which it increases by multiplying the rate at which particle 1 encounters field particles times $(\Delta p_\perp)^2$.

The rate of encounters with cross section b is $n_2 v_1 \times 2\pi b\, db$, i.e., number of targets in the field times velocity with which particle 1 moves through them times area with impact parameter between b and $b + db$. Here we're making the simplifying assumption that v_1 is much larger than the mean velocity of the field particles, so that we don't have to worry about integrating over the Maxwellian distribution they present, i.e., $v_1 \gg \overline{v}$; properly integrating over relative velocities just introduces a factor of order unity difference. Thus we get a rate of change for $(\Delta p_\perp)^2$

$$\left\langle \frac{d}{dt} \left(\Delta p_\perp\right)^2 \right\rangle = \int_{b_{\min}}^{b_{\max}} n_2 v_1 2\pi b \left(\frac{2 Z_1 Z_2 e^2}{b v_1}\right)^2 db = \frac{8\pi n_2 Z_1^2 Z_2^2 e^4}{v_1} \int_{b_{\min}}^{b_{\max}} \frac{db}{b}. \tag{3}$$

Clearly we cannot take $b_{\min} = 0$ or $b_{\max} = \infty$ without the integral diverging. For the minimum impact parameter to consider, we can adopt the impact parameter for which the impulse approximation used to compute $\Delta p_\perp$ fails. If the initial kinetic energy in the center of mass frame is E, this failure occurs when the interaction energy is comparable to E – if this is the case, then clearly we cannot ignore the deflection of the particles during the encounter. Thus we take $b_{\min} = Z_1 Z_2 e^2/E$. For the maximum, the plasma will shield charges on size scales longer than the Debye length,

$$L_D = \left(\frac{kT}{4\pi n_e e^2}\right)^{1/2}, \tag{4}$$

where n_e is the free electron density, and this will cut off the Coulomb force from larger distances. Thus we take $b_{\max} = L_D$, and we have

$$\left\langle \frac{d}{dt} (\Delta p_\perp)^2 \right\rangle = \frac{8\pi n_2 Z_1^2 Z_2^2 e^4}{v_1} \ln \Lambda, \tag{5}$$

where $\ln \Lambda$ is known as the Coulomb logarithm, and has the value

$$\ln \Lambda = \ln \left[\frac{E}{kT} \frac{(kT)^{3/2}}{(4\pi n_e)^{1/2} Z_1 Z_2 e^2} \right] = 22.1 + \ln \left[\left(\frac{E}{kT} \right) \left(\frac{T}{10^4 \text{ K}} \right)^{3/2} \left(\frac{\text{cm}^{-3}}{n_e} \right) \right] \tag{6}$$

Note that we made some very rough approximations in computing $b_{\min}$ and $b_{\max}$, but these enter the result only logarithmically.

We are now in a position to answer the question of on what length scales we can treat a plasma as a fluid. The characteristic time for the random walk produced by lots of little kicks $\Delta p_\perp$ to randomise an initial velocity v_1, known as the deflection time, is

$$t_{\text{defl}} = \frac{(m_1 v_1)^2}{\langle (d/dt)(\Delta p_\perp)^2 \rangle} = \frac{m_1^2 v_1^3}{8\pi n_2 Z_1^2 Z_2^2 e^4 \ln \Lambda}, \tag{7}$$

and the distance the particle travels in this time, the effective mean free path, is

$$\lambda_{\text{mfp}} = v_1 t_{\text{defl}} = \frac{m_1^2 v_1^4}{8\pi n_2 Z_1^2 Z_2^2 e^4 \ln \Lambda}. \tag{8}$$

If we consider electrons being deflected either by other electrons or by protons, and plug in a velocity corresponding to a kinetic energy $(3/2)kT$ (not fully consistent with our choice to take v_1 much larger than the thermal energy, but we're only after an order of magnitude estimate here), we have

$$\lambda_{\text{mfp}} = 5 \times 10^{12} \left(\frac{m_1}{m_e} \right)^2 \left(\frac{T}{10^4 \text{ K}} \right)^2 \left(\frac{0.1 \text{ cm}^{-3}}{n_2} \right) \left(\frac{25}{\ln \Lambda} \right) \text{ cm}. \tag{9}$$

Thus on size scales larger than ~ 1 AU, for densities of ~ 0.1 cm^{-3} and temperatures $\sim 10^4$ K, we may consider the electrons in a plasma to be a fluid.

C. Thermal equilibration

We can use the same sort of approach to estimate the time it will take for particles to reach thermal equilibrium. Instead of asking about the deflection of a particle by its random walk in momentum space, we can now ask about how its energy changes due to these deflections. Suppose particle 1 has initial velocity v_1, so its kinetic energy is $(1/2)m_1 v_1^2$, and again assume v_1 is much greater than the thermal velocities of the field particles. Each time particle 1 undergoes an encounter, it gives momentum $\Delta p_\perp$ to the field particle, and as a result its energy decreases by $(\Delta p_\perp)^2/(2m_2)$. The time required for such encounters to completely deplete particle 1's excess energy and make it into a field particle is

$$t_{\text{loss}} = \frac{m_1 v_1^2}{\langle (d/dt)(\Delta p_\perp)^2 / m_2 \rangle} = \frac{m_1 m_2 v_1^3}{8\pi n_2 Z_1^2 Z_2^2 e^4 \ln \Lambda}. \tag{10}$$

If we ask how long it will take encounters between fast electrons with a speed corresponding to a temperature T_e, and a sea of protons with number density n_p, to slow down the electrons, we get

$$t_{\text{loss}} = 0.4 \times \left(\frac{T_e}{10^4\ \text{K}}\right)^{3/2} \left(\frac{\text{cm}^{-3}}{n_p}\right) \left(\frac{25}{\ln \Lambda}\right)\ \text{Myr}. \tag{11}$$

Thus hot electrons make take ~ 1 Myr to slow down due to encounters with protons.

This makes an important point. Due to the difference in mass between protons and electrons, the electrons and protons exchange energy only slowly – each deflection of an electron involves a lot of momentum, but gives the proton very little energy because the proton velocity changes little. As a result, the electrons will thermalise with respect to each other quickly, but may not reach the same temperature as the protons for a long time. A gas in this state is referred to as a two-temperature plasma, because the electrons and protons each have a well-defined Maxwellian velocity distribution, but at different temperatures.

II. The law of mass action and the principle of detailed balance

Now that we have understood the basics of when we can treat the dynamics of the ISM in the fluid approximation, we now turn to the statistical and thermal mechanics of the ISM. We will spend the rest of this class deriving and exploring two important results that we will repeatedly use in the following weeks: the law of mass action and the principle of detailed balance.

A. The Boltzmann and Gibbs distributions

Let us begin our discussion with a brief review of some material from undergraduate thermodynamics. Suppose we consider a system which has a number of possible energy levels E_i, ordered so that E_0 is the lowest energy state. Each level has degeneracy g_i, meaning that there may be two distinct quantum states with identical energies, and g_i counts the number of such states with identical energy. The question we wish to ask is: for a system at temperature T, what is the probability that, at any given time, we will find that the system in question is in state i?

The answer to this question is a fundamental result in thermodynamics, the Boltzmann distribution. The result, which we'll simply quote since you have certainly seen it derived before, is that

$$P() = g_i \frac{e^{-E_i/kT}}{Z(T)}, \tag{12}$$

where

$$Z(T) = \sum g_i e^{-E_i/kT} \tag{13}$$

is called the partition function. Note that this is the probability of having a particular energy E_i; if we want the probability of being in a particular distinct state, we can drop the factor g_i.

The chemical potential arises when we generalise our question by asking about a system where the number of particles in the system is not fixed. Let us consider our system to be a volume of space containing a number of particles N, and let $E_i(N)$ represent the possible energy levels of the system at a time when it contains exactly N particles. We can now ask the question: given a system temperature T, what is the probability that, at any time we observe it, the system contains exactly N particles and is in state i with energy $E_i(N)$?

The answer to this more general question is given by the Gibbs distribution, and, again, we will simply quote the result rather than derive it. The answer is

$$P(i,N) = g_i \frac{e^{[N\mu - E_i(N)]/kT}}{\zeta(N,T)} \equiv g_i \frac{\lambda^N e^{-E_i(N)/kT}}{\zeta(\mu,T)} \tag{14}$$

where

$$\zeta(\mu,T) = \sum_N \sum_i g_i e^{[N\mu - E_i(N)]/kT} \equiv \sum_N \sum_i g_i \lambda^N e^{-E_i(N)/kT} \tag{15}$$

is called the Gibbs sum, or the grand sum, and the sums run over all possible particle numbers N and energy levels i. For convenience we have defined $\lambda = e^{\mu/kT}$, the absolute activity. The quantity μ is called the chemical potential, and it describes the change in the free energy of the system as the number of particles is changed.

B. Ideal gases

Of course both of these laws are useful only to the extent that we can actually write down the energy levels and the chemical potential for the system in which we are interested. For the purposes of applications in the ISM and IGM, the type of gas in which we are interested is a classical, ideal one. By “classical” we mean that the expected number of atoms per quantum state is $\ll 1$, and by“ideal” we mean that the inter-particle separation is large enough that we can neglect interactions between individual atoms or molecules when calculating their internal energy levels – in effect each particle sits alone in a vacuum as far is its internal energy levels are concerned. Given the low densities of gases in the ISM, both the classical and the ideal approximations are very reasonable.

To calculate the partition function and the chemical potential, let us start by considering a single atom or molecule of mass m located in a box of size l. For a particle with no internal structure, the quantum state of a particle in the box is described by three quantum numbers (n_x, n_y, n_z), and that the energy of each state is given by

$$E_{\rm trans} = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2). \tag{16}$$

For atoms that do have internal structure, we must add a fourth quantum number i, describing its internal state. As before, let E_i be the energy of this internal state. The partition function is therefore

$$Z(T) = \sum_{n_x}\sum_{n_y}\sum_{n_z}\sum_i g_i e^{-(E_{\rm trans}+E_i)/kT} = \left(\sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-E_{\rm trans}/kT}\right)\cdot\left(\sum_i g_i e^{-E_i/kT}\right) \tag{17}$$

The first quantity in parentheses we refer to as the translational partition function $Z_{\rm trans}$, and the second is the internal partition function $z_{\rm int}$ (by convention usually written with a small z). Clearly the total partition function is just a product of the two.

The translational partition function is relatively easy to evaluate:

$$\begin{aligned} Z_{\rm trans}(T) &= \sum_{n_x}\sum_{n_y}\sum_{n_z}\exp\left[-\frac{h^2}{8ml^2kT}\left(n_x^2+n_y^2+n_z^2\right)\right] && (18)\\ &= \left[\sum_n \exp\left(-\frac{h^2n^2}{8ml^2kT}\right)\right]^3 && (19)\\ &\approx \left[\int_0^\infty \exp\left(-\frac{h^2n^2}{8ml^2kT}\right)dn\right]^3 && (20)\\ &= \frac{(2\pi mkT)^{3/2}}{h^3}V, && (21)\end{aligned}$$

where $V = l^3$. In the third step we approximated the sum by an integral, which is reasonable when the system is not extremely cold and most particles are in high n levels.

Since $Z_{\rm trans} \propto V$, for dilute gases we often define the partition function per unit volume

$$f(T) = \frac{Z(T)}{V} = \frac{(2\pi mkT)^{3/2}}{h^3}z_{\rm int}(T). \tag{22}$$

What about the chemical potential of an ideal gas? That is straightforward as well; we can infer the chemical potential by demanding that we get the right number of particles. The argument proceeds as follows.

Let us consider a volume V of interest, and within that consider a "system" consisting of a single set of translational quantum numbers $\mathbf{n} = (n_x, n_y, n_z)$. An atom with this particular set of translational quantum numbers can also have an internal quantum number i, and can therefore have a total energy $E = E_{\rm trans} + E_i$.

Under the assumption that we are dealing with a classical gas, the expected number of particles with translational quantum number $\mathbf{n}$ is $\ll 1$, and we can therefore neglect the possibility that the number of particles is greater than 1. With this approximation, the Gibbs sum is given by

$$\zeta(\mu, T) = 1 + \lambda\sum_i g_i e^{-(E_{\rm trans}+E_i)/kT} \tag{23}$$

$$= \quad 1 + \lambda e^{-E_{\text{trans}}/kT} \sum_i g_i e^{-E_i/kT} \tag{24}$$

$$= \quad 1 + \lambda e^{-E_{\text{trans}}/kT} z_{\text{int}}(T) \tag{25}$$

The first term comes from the possibility that there are 0 particles present, in which case the energy is of course also zero. The second, much smaller, term comes from the possibility that there is 1 particle present. The probability that there is exactly 1 particle with translational quantum numbers **n** is then

$$P(\mathbf{n}, 1) = \frac{\lambda e^{-E_{\text{trans}}/kT} z_{\text{int}}(T)}{1 + \lambda e^{-E_{\text{trans}}/kT} z_{\text{int}}(T)} \approx \lambda e^{-E_{\text{trans}}/kT} z_{\text{int}}(T). \tag{26}$$

We are now almost at the desired result. We have computed the probability that there is exactly 1 particle in a given translational quantum state **n**, so the total expected number of particles present in all quantum states is simply the sum of this probability over all possible states:

$$\langle N \rangle = \lambda z_{\text{int}}(T) \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-E_{\text{trans}}/kT}. \tag{27}$$

The sum is simply the translational partition function that we evaluated above, and thus the expected number of particles present is

$$\langle N \rangle = \lambda z_{\text{int}}(T) \left[\frac{(2\pi mkT)^{3/2}}{h^3} V \right] \tag{28}$$

We therefore have

$$\lambda = e^{\mu/kT} = \frac{nh^3}{(2\pi mkT)^{3/2} z_{\text{int}}(T)}, \tag{29}$$

or, equivalently,

$$\mu = kT \ln \frac{nh^3}{(2\pi mkT)^{3/2} z_{\text{int}}(T)}. \tag{30}$$

This gives the chemical potential of an ideal, classical gas.

An important point to note is that this applies to each distinct chemical species. Each species has its own number density, its own internal partition function, and its own chemical potential.

C. The law of mass action

Now that we have that formal throat-clearing out of the way, we are prepared to derive our interesting and important result: the law of mass action. Let us consider a region where there are a number of chemical species present; we denote the species of interest A_j, and we denote the number density of species A_j by n_j. The distinct states can be chemically different atoms or molecules, they can be atoms of molecules in distinct ionisation states, or they can even be atoms or molecules in distinct quantum states. The result is powerful enough that it doesn't matter.

Now let us consider some reaction that is capable of changing members of one species into members of another species. We will denote this reaction in the following form:

$$\nu_1 A_j + \nu_2 A_2 + \cdots + \nu_l A_l = \sum_j \nu_j A_j = 0. \tag{31}$$

The coefficients ν are known as the stoichiometric factors, and they simply specify how the numbers of the different species are related. For example, consider the reaction

$$2H_2 + O_2 \leftrightarrow 2H_2O. \tag{32}$$

In this case $A_1 = H_2$, $A_2 = O_2$, $A_3 = H_2O$, $\nu_1 = 2$, $\nu_2 = 1$, and $\nu_3 = -2$. The meaning of this is that every forward reaction destroys 2 H_2 molecules and 1 O_2 molecule, and produces 2 H_2O molecules.

Suppose that the system is in chemical equilibrium, so that the total number densities n_j are constant. In this case, the change in free energy that occurs when a reaction takes place must be zero, since, if it were non-zero, either the forward or the backward reaction would occur spontaneously. However, recall that the chemical potential is simply the change in free energy associated with changes in the numbers of particles present. If a single forward reaction occurs, then ν_j particles of species j appear (if ν_j is positive) or disappear (if it is negative), and the change in free energy is therefore

$$\sum_j \nu_j \mu_j. \tag{33}$$

The argument we have just made implies that, in chemical equilibrium, this sum is zero.

Substituting in the chemical potential we have derived for ideal gases, we can therefore write

$$\begin{aligned} 0 &= \sum_j \nu_j kT \ln \frac{n_j h^3}{(2\pi m_j kT)^{3/2} z_{\mathrm{int},j}(T)} && (34) \\ \sum_j \ln n_j^{\nu_j} &= \sum_j \ln \left[\frac{(2\pi m_j kT)^{3/2}}{h^3} z_{j,\mathrm{int}}(T) \right]^{\nu_j} && (35) \\ \prod_j n_j^{\nu_j} &= \prod_j \left[\frac{(2\pi m_j kT)^{3/2}}{h^3} z_{j,\mathrm{int}}(T) \right]^{\nu_j} \equiv K(T) && (36) \end{aligned}$$

This final result is known as the law of mass action. The quantity $K(T)$ is known as the reaction constant.

It is worth stepping back to appreciate the generality and power of this result. This power comes from the fact that the reaction constant is a function only of the temperature and the internal properties of the various reaction constituents (their partition functions and masses). This means that, for any chemical reaction involving arbitrary numbers of components, we can calculate the ratios of the number densities of the various constituents in LTE even if we know nothing other than the internal level structures and masses of the various participants in the reaction.

D. Detailed balance

The best way to appreciate the generality and power of the law of mass action is to apply it, and one of the immediate applications is known as the principle of detailed balance, which allows us to relate the rate of forward and backward reaction rate coefficient.

Suppose we have reaction

$$R_1 + R_2 + \cdots + R_M \leftrightarrow P_1 + P_2 + \cdots + P_N, \tag{37}$$

where we have simplified the algebra a bit by assuming that we will use only one of each component, so all the ν_j coefficients are $+1$ or -1. From our discussion in the last class, we know that the rate at which the left-to-right reaction proceeds is given by

$$\text{reactions cm}^{-3} = k_{\text{LHS}} n_{R_1} n_{R_2} \cdots n_{R_M} = k_{\text{LHS}} \prod n_{R_i} \tag{38}$$

and similarly for the right-hand-side. In equilibrium these two rates must balance:

$$\frac{k_{\text{RHS}}}{k_{\text{LHS}}} = \frac{\prod_{i=1}^{M} n_{R_i}}{\prod_{j=1}^{N} n_{P_j}} \tag{39}$$

However, notice that the ratio of products on the right hand side is just $\prod_j n_j^{\nu_j}$. We can therefore invoke the law of mass action, which tells us that, if the system is in LTE, this product is given by

$$\frac{k_{\text{RHS}}}{k_{\text{LHS}}} = \frac{\prod_{i=1}^{M} n_{R_i}}{\prod_{j=1}^{N} n_{P_j}} = \left[\frac{(2\pi kT)^{3/2}}{h^3}\right]^{M-N} \left[\frac{\prod_{i=1}^{M} m_{R_i}}{\prod_{j=1}^{N} m_{P_j}}\right]^{3/2} \frac{\prod_{i=1^M} z_{\text{int}}(R_i, T)}{\prod_{j=1^N} z_{\text{int}}(P_j, T)}. \tag{40}$$

This is the principle of detailed balance.

An important point to make is that, even though we derived this result by considering what happens for a system in LTE, the restrictions on the rate coefficients are general. They apply even to a system that is not in LTE. Recalling the last class, the rate coefficients only depend on microphysical cross sections, which are independent of whether the system is in LTE, and the Maxwellian velocity distribution of the colliding particles. Therefore the only restriction on the principle of detailed balance is that it applies only to systems where the colliding particles have a Maxwellian velocity distribution. As we saw last class, that restriction is generally satisfied on any reasonable size scale in the ISM, even if the gas is far from LTE.

III. Applications of detailed balance and the law of mass action

A. Collision rates

The principle of detailed balance is mathematically nasty-looking, but it contains a critical result: we have been able to write the ratio of the rate coefficients solely in terms of the temperature and the internal properties of the reactants. As a further subtlety, nothing we have done in our derivation has made any assumptions about what the reactants have to be. They can be atoms, molecules, or individual quantum states of those atoms or molecules.

As a first demonstration of the utility of this result, consider something from last class: collisional excitation or de-excitation of an atom or molecule. Suppose we have a species X which can be in two states ℓ or u, which we denote $X(\ell)$ or $X(u)$. Collisions between species X and another species Y cause collisional excitations or de-excitations between the states, so the reaction is

$$X(\ell) + Y \leftrightarrow X(u) + Y. \tag{41}$$

Applying the principle of detailed balance to this, we obtain

$$\frac{k_{u\ell}}{k_{\ell u}} = \frac{z_{\mathrm{int}}(X(\ell), T)}{z_{\mathrm{int}}(X(u), T)}, \tag{42}$$

where $k_{u\ell}$ is the rate coefficient for the $u \to \ell$ transition, and similarly for $k_{\ell u}$. Notice that there have been numerous cancellations. The first term in square brackets in the law of detailed balance cancels because $M = N$, and the second term cancels because the products of the masses on the left and right sides of the reaction are the same. In addition, since species Y is unchanged in the reaction, its partition function cancels as well.

We can further simplify by noting that the partition functions of $X(u)$ and $X(\ell)$ are trivial, since each corresponds to a single quantum state. If E_u and E_ℓ are the energies of the upper and lower states, and g_u and g_ℓ are their degeneracies, then $z_{\mathrm{int}}(X(\ell), T) = g_\ell e^{-E_\ell/kT}$ and $z_{\mathrm{int}}(X(u), T) = g_u e^{-E_u/kT}$. Thus we have

$$\frac{k_{u\ell}}{k_{\ell u}} = \frac{g_\ell}{g_u} e^{E_{u\ell}/kT}. \tag{43}$$

We have therefore related the rates of collisional excitation and de-excitation for a given species solely in terms of the temperature, the degeneracies of the levels, and the energy difference between them.

This result applies only if the particles have a Maxwellian velocity distribution, which is pretty much everywhere. However, we can derive something even more general as applied to the microphysical cross sections. Recall from last class that

$$k_{u\ell} = \sqrt{\frac{8kT}{\pi\mu}} \int_0^\infty x e^{-x} \sigma_{u\ell}(E)\, dx = \sqrt{\frac{8kT}{\pi\mu}} \int_0^\infty \frac{E}{kT} e^{-E/kT} \sigma_{u\ell}(E)\, \frac{dE}{kT} \tag{44}$$

where μ is the reduced mass of the system. Similarly,

$$k_{\ell u} = \sqrt{\frac{8kT}{\pi\mu}} \int_{E_{u\ell}}^\infty \frac{E}{kT} e^{-E/kT} \sigma_{u\ell}(E)\, \frac{dE}{kT}, \tag{45}$$

where the integral starts from a lower limit of $E_{u\ell}$ because lower energy collisions obviously do not have enough energy to induce an upward transition between states ℓ and u.

Plugging these two expressions into the relationship we have just derived, we have

$$\frac{\int_0^\infty E e^{-E/kT} \sigma_{u\ell}(E)\, dE}{\int_{E_{u\ell}}^\infty E e^{-E/kT} \sigma_{\ell u}(E)\, dE} = \frac{g_\ell}{g_u} e^{E_{u\ell}/kT}. \tag{46}$$

Re-arranging, we have

$$\int_{E_{u\ell}}^\infty E e^{-E/kT} \sigma_{\ell u}(E)\, dE = \int_0^\infty \frac{g_u}{g_\ell} E e^{-(E+E_{u\ell})/kT}\, \sigma_{u\ell}(E) dE. \tag{47}$$

For the integral on the left, let us make a change of variable $E' = E - E_{u\ell}$. This gives

$$\int_0^\infty (E' + E_{u\ell}) e^{-(E'+E_{u\ell})/kT} \sigma_{\ell u}(E' + E_{u\ell})\, dE = \int_0^\infty \frac{g_u}{g_\ell} E e^{-(E+E_{u\ell})/kT}\, \sigma_{u\ell}(E) dE. \tag{48}$$

Clearly these two integrals can be equal for arbitrary T, as they must be, only if

$$(E + E_{u\ell}) \sigma_{\ell u}(E + E_{u\ell}) = \frac{g_u}{g_\ell} E \sigma_{u\ell}(E). \tag{49}$$

This rule applies to the energy-dependent cross section itself, which is a function solely of the microphysical properties of the atoms in question. Thus we have managed to constrain even atomic physics based on our statistical equilibrium arguments.

B. The Saha equation

A second important application of detailed balance and the law of mass action is to ionisation and recombination processes. Consider an ionisation-recombination reaction in which a species X with a charge $+r+1$ recombines with an electron, reducing its charge to $+r$:

$$X^{+r+1} + e^- \leftrightarrow X^{+r} \tag{50}$$

Note that r may be zero.

Applying the law of mass action, we have

$$\frac{n_e n_{X^{+r+1}}}{n_{X^{+r}}} = \left[\frac{(2\pi m_e kT)^{3/2}}{h^3}\right] \frac{2 z_{\rm int}(X^{+r+1}, T)}{z_{\rm int}(X^{+r}, T)}. \tag{51}$$

The factor of 2 in the numerator of the second term comes from the partition function of the electron, which is 2, since the electron has two spin states that have equal energy.

If the temperature is low enough that each of the ionised species is likely to be in its ground state, then we can replace the sums in the partition functions by just their first terms. In other words, if $e^{-E/kT} \ll 1$ for all the levels above the ground level, then we can write

$$z_{\text{int}}(X^{+r}, T) \approx g_{r,1} e^{-E_{r,1}/kT} \qquad \text{and} \qquad z_{\text{int}}(X^{+r+1}, T) \approx g_{r+1,1} e^{-E_{r+1,1}/kT}, \tag{52}$$

where the subscript $r, 1$ refers to the ground state of the atom with charge r, and the subscript $r+1, 1$ refers to the ground state of the atom with charge $r+1$.

Substituting this in, we obtain

$$\frac{n_e n_{X^{+r+1}}}{n_{X^{+r}}} = \left[\frac{(2\pi m_e kT)^{3/2}}{h^3}\right] \frac{g_{r+1,1}}{g_{r,1}} e^{-I_r/kT}, \tag{53}$$

where $I_r = E_{r+1,1} - E_{r,1}$ is the ionization potential of species X^{+r}. This result is known as the Saha equation. For hydrogen, the degeneracy of the neutral state is 4 (2 possible proton spins times 2 possible electron spins) and the degeneracy of the ionised state is 2 (2 possible proton spins), so as applied to H the Saha equation gives

$$\frac{n_e n_{\text{H}^+}}{n_{\text{H}^0}} = \frac{(2\pi m_e kT)^{3/2}}{h^3} e^{-I_{\text{H}}/kT}. \tag{54}$$

It is important to emphasise that the Saha equation applies only in LTE, since it relies on the law of mass action. Thus it is a good approximation for high density environments (say inside a star), but generally not in the ISM.