

# Statistical mechanics and Thermodynamic equilibrium. Part 2

- Partition functions
- The Law of Mass Action
- Ionization and recombination
- Saha Equation.
- Principle of detailed balance
- Excitation temperature

Reference book: B. Draine, *The physics of the Interstellar and Integalactic medium*, chapter 3

# Partition functions

Although the ISM is far from thermodynamical equilibrium, the methods of statistical mechanics and thermodynamics are needed to understand the processes which develop in the ISM and shape the medium.

- Partition functions

Consider a physical system (e.g., atoms in a finite volume  $V$ ) which can exchange energy with a «heat reservoir» at temperature  $T$ . The theory of statistical mechanics defines the **partition function** (being  $s$  a given state of the system and  $E$  its total energy):

$$Z(T) \equiv \sum_s e^{-E(s)/kT}$$

For dilute gas, this can be factored out as:  $Z(T) = Z_{tran}(T) \times z_{int}(T)$  (translational and internal) .

Example: let's consider a **single atom**. Labeling with index  $i = 0, 1, 2, \dots$  the internal energy levels of the system, its total energy is (being  $p$  the linear momentum and  $M_X$  the atom mass):

$$E(X_i) = \frac{p^2}{2M_X} + E_i$$

$$Z_{tran}(X; T) = \frac{V}{h^3} \int_0^\infty 4\pi p^2 dp e^{-p^2/(2M_X kT)} = \frac{(2\pi M_X kT)^{3/2}}{h^3} V \quad (\text{integral over the 6-dimensional phase space; } h^3 = \text{cell size})$$

$$z_{int}(X; T) \equiv \sum_i g_i e^{-E_i/kT} \quad g_i = \text{multiplicity or } \textit{degeneracy} \text{ of the } E_i \text{ internal energy level.}$$

[*Example:* a single electron has two spin states, both with  $E_i = 0$ , so that  $z_{int} = 2$ .]

We use the **partition function per unit volume**,

$$f(X, T) \equiv \frac{Z}{V} = \left[ \frac{(2\pi M_X kT)^{3/2}}{h^3} \right] z_{int}(X; T)$$

## The law of mass action

Consider a chemical reaction  $A+B \longleftrightarrow C$ . From statistical mechanics, in LTE one has (being  $n(X)$  number density of the  $X$  species):

$$\frac{n_{\text{LTE}}(C)}{n_{\text{LTE}}(A)n_{\text{LTE}}(B)} = \frac{f(C)}{f(A)f(B)}$$

For arbitrary number of products and reactants,  $R_1 + R_2 + \dots + R_M \leftrightarrow P_1 + P_2 + \dots + P_N$ , the law of mass action is:

$$\frac{\prod_{j=1}^N n_{\text{LTE}}(P_j)}{\prod_{i=1}^M n_{\text{LTE}}(R_i)} = \frac{\prod_{j=1}^N f(P_j)}{\prod_{i=1}^M f(R_i)} = \left[ \frac{(2\pi kT)^{3/2}}{h^3} \right]^{N-M} \left[ \frac{\prod_{j=1}^N M(P_j)}{\prod_{i=1}^M M(R_i)} \right]^{3/2} \frac{\prod_{j=1}^N z_{\text{int}}(P_j; T)}{\prod_{i=1}^M z_{\text{int}}(R_i; T)}$$

[NOTE: Reactants  $R_i$  and products  $P_j$  can be different species, or even different internal quantum states of atoms/molecules.]

For each reactant and product, we choose their reference states  $R_{i,0}$  and  $P_{j,0}$  so that:

$$E(R_{1,0} + \dots + R_{M,0}) + \Delta E = E(P_{1,0} + \dots + P_{N,0})$$

$\Delta E > 0$  means endothermic reaction.

With this definition,

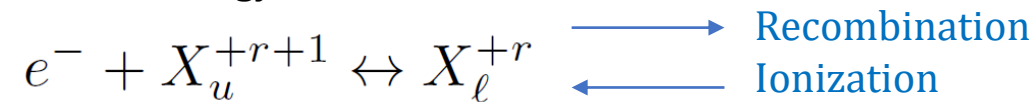
$$\frac{\prod_{j=1}^N z_{\text{int}}(P_j; T)}{\prod_{i=1}^M z_{\text{int}}(R_i; T)} = e^{-\Delta E/kT} \frac{\prod_{j=1}^N \sum_s g(P_{j,s}) e^{-[E(P_{j,s}) - E(P_{j,0})]/kT}}{\prod_{i=1}^M \sum_s g(R_{i,s}) e^{-[E(R_{i,s}) - E(R_{i,0})]/kT}}$$

and therefore

$$\frac{\prod_{j=1}^N n_{\text{LTE}}(P_j)}{\prod_{i=1}^M n_{\text{LTE}}(R_i)} = \left[ \frac{(2\pi kT)^{3/2}}{h^3} \right]^{N-M} \left[ \frac{\prod_{j=1}^N M(P_j)}{\prod_{i=1}^M M(R_i)} \right]^{3/2} \times e^{-\Delta E/kT} \frac{\prod_{j=1}^N \sum_s g(P_{j,s}) e^{-[E(P_{j,s}) - E(P_{j,0})]/kT}}{\prod_{i=1}^M \sum_s g(R_{i,s}) e^{-[E(R_{i,s}) - E(R_{i,0})]/kT}} .$$

### Application: Ionization and Recombination in LTE

The law of mass action can be applied to the ionization/recombination balance, in LTE. Consider a species  $X^{+r}$  at a specific internal energy level  $\ell$  and a species  $X^{+r+1}$  at a specific internal energy level  $u$ :



Here,  $N = 1$  (product),  $M = 2$  (reactants). The masses of  $X^{+r}$  and  $X^{+r+1}$  are  $\sim$ the same. The law of mass action then gives:

$$\underbrace{n_{\text{LTE}}(X_\ell^{+r})}_{\text{Product}} = \frac{h^3}{2(2\pi m_e kT)^{3/2}} \underbrace{n(X_u^{+r+1}) n_e}_{\text{reactants}} \frac{g(X_\ell^{+r})}{g(X_u^{+r+1})} e^{-(E_{r,\ell} - E_{r+1,u})/kT}$$

Electron degeneracy

The **overall** balance of recombination and ionization between the species  $X^{+r+1}$  and  $X^{+r}$  ,  $e^- + X^{+r+1} \leftrightarrow X^{+r}$  is obtained by summing over all the internal states  $\ell$  . From the law of mass action,

$$\frac{n_{\text{LTE}}(X^{+r})}{n_{\text{LTE}}(e^-)n_{\text{LTE}}(X^{+r+1})} = \frac{h^3}{(2\pi m_e kT)^{3/2}} \frac{\sum_j g_{r,j} e^{-E_{r,j}/kT}}{2 \sum_j g_{r+1,j} e^{-E_{r+1,j}/kT}}$$

↑  
Sum over internal states

At sufficiently low T, we retain only the lowest energy state in each sum: in this approximation, we obtain the **Saha Equation**,

$$\frac{n_{\text{LTE}}(e^-)n_{\text{LTE}}(X^{+r+1})}{n_{\text{LTE}}(X^{+r})} \approx \frac{2(2\pi m_e kT)^{3/2}}{h^3} \frac{g_{r+1,0}}{g_{r,0}} e^{-\Phi_r/kT}$$

where  $\Phi_r = E_{r+1,0} - E_{r,0}$  = ionization energy of species X ( energy to extract one  $e^-$  from the fundamental state of X).

**Example: Hydrogen atom.** Here,  $g_{r,0}$  is the multiplicity of the fundamental state of the neutral atom (H can only be ionized once). So,  $g_{r,0}$  describes the neutral H in the state (1s): the multiplicity is  $2 \times 2 = 4$  (both the proton and the electron have only one degree of freedom, the spin, which can be up or down). For  $g_{r+1,0}$  , only the proton remains in  $H^+$ , the ionized H, so that  $g_{r+1,0} = 2$  . The H ionization energy is  $I_H = 13.60$  eV:

$$\frac{n_{\text{LTE}}(e^-)n_{\text{LTE}}(H^+)}{n_{\text{LTE}}(H^0)} = \frac{(2\pi m_e kT)^{3/2}}{h^3} e^{-I_H/kT}$$



LTE (and law of mass action , and Saha's eq., not valid in most ISM, electromagnetic field far from a Black body!

## Principle of Detailed Balance and ratios of Rate Coefficients in LTE.

In a typical *balanced* chemical reaction between species A,B,P,Q with stoichiometric coefficients a,b,p,q:  $aA + bB \rightarrow pP + qQ$ ,

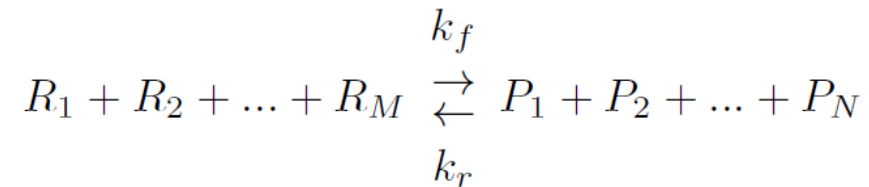
the velocity is:  $\text{Rate} \equiv \frac{1}{\alpha} \lim_{\Delta t \rightarrow 0} \frac{\Delta[X]}{\Delta t} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt} = \frac{1}{q} \frac{d[Q]}{dt}$

The **rate law** is an empirical expression relating the reaction rate to a constant  $k$  and to the concentration of reactants.

In the example  $aA + bB \rightarrow pP + qQ$ , the rate law reads: **Rate direct reaction** =  $k_f [A]^a [B]^b$  and **Rate inverse reaction** =  $k_r [P]^p [Q]^q$ .

The **principle of detailed balance** is formulated for kinetic systems which are decomposed into elementary processes (collisions, or steps, or elementary reactions): *at equilibrium, each elementary process should be equilibrated by its reverse process.*

Consider a general reaction:



At the equilibrium, the number of reactions from reactants R to products P, per unit volume and unit time, is equal to the number of reverse reactions, per unit volume and time. The **reaction rates**  $k_f$  and  $k_r$  measure the corresponding velocity:

$$k_f \prod_{i=1}^M n_{LTE}(R_i) = k_r \prod_{j=1}^N n_{LTE}(P_j)$$

# Excitation temperature

$$z_{int}(X; T) \equiv \sum_i g_i e^{-E_i/kT}$$

The excitation temperature of level u relative to level l is defined :

$$\frac{n_{up}}{n_{low}} = \frac{g_{up}}{g_{low}} e^{-\frac{(E_{up}-E_{low})}{kT_{ex,ul}}}$$

or

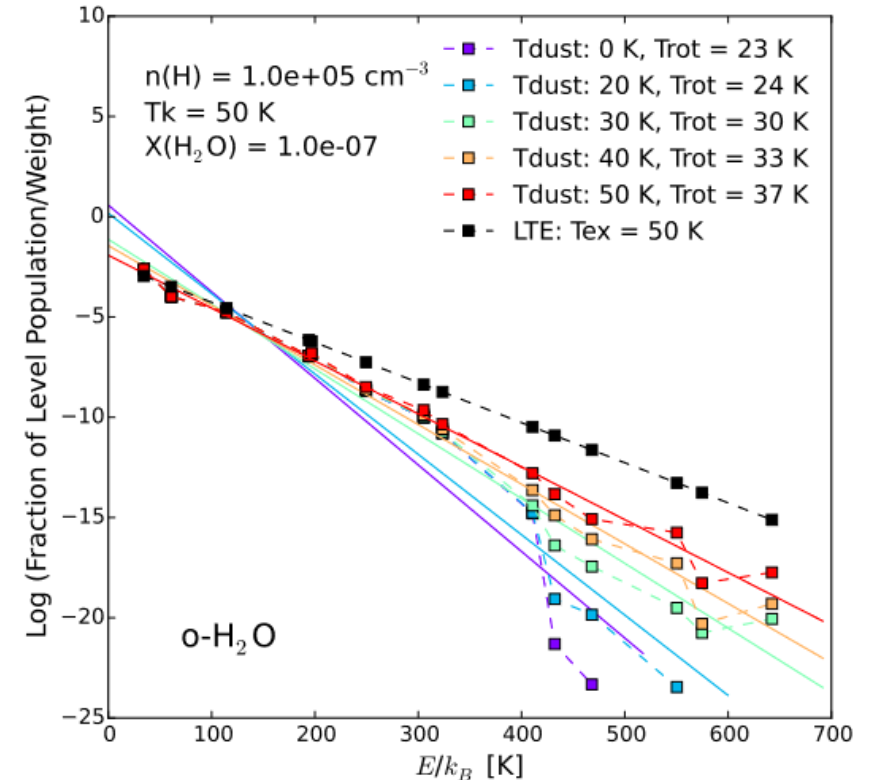
$$T_{ex,ul} \equiv \frac{E_{ul}/k}{\ln\left(\frac{n_l/g_l}{n_u/g_u}\right)}$$

In LTE,  $T = T_{kinetic} = T_{excitation}$ , same for all levels.

Coupling between  $T_{kinetic}$  and  $T_{excitation}$  can occur through **collisions**.

We achieve kinetic equilibrium with collisions between atoms or molecules.

If particles have internal degrees of freedom, the kinetic energy can produce excitation, coupling the two temperatures. If the kinetic temperature is higher than the excitation temperature, collisions drive the particles towards higher energy states, thus raising the excitation temperature of this transition.



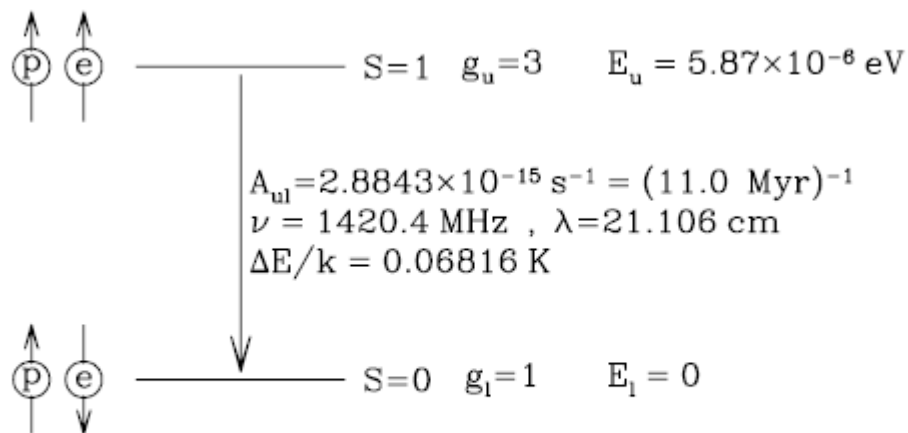
Liu et al. The Astrophysical Journal, 846:5 (2017)

## Example. The 21 cm HI line.

The electron in the electronic ground state ( $1s$ ) of atomic hydrogen can have its spin either parallel or antiparallel to the spin of the proton. The coupling of the electron's magnetic moment to the magnetic field produced by the magnetic moment of the proton results in "hyperfine splitting" of the parallel and antiparallel spin states.

The antiparallel spin state (with degeneracy  $g = 1$ ) has the lower energy, which we take to be  $E = 0$ . The parallel spin state (with total spin  $S = 1$ , and degeneracy  $g = 2S + 1 = 3$ ) has an energy  $E_u - E = 5.87 \times 10^{-6}$  eV. When the electron drops to the ground state, the electron spin flips, and a photon is emitted with a wavelength  $\lambda = 21.11$  cm.

Because of the small energy splitting between these two spin states, the CMB by itself is able to populate the upper level. We expect  $T_{exc} \equiv T_{spin} \gg 0.068$  K



$$\frac{n_{up}}{n_{low}} = 3 e^{-\frac{h\nu_{ul}}{kT_{spin}}} = 3 e^{-\frac{0.068 \text{ K}}{T_{spin}}} \sim 3$$

Figure 8.1 Hyperfine splitting of the  $1s$  ground state of atomic H (Gould 1994).