Chapter 7

The Early Universe: Neutrinos, Nucleosynthesis and Recombination

With telescopes we can look all the way back to the time when the CMB was released, at $z = 1100$, i.e. 0.3 million years after the Big Bang. Unfortunately the CMB blocks our view of what happened earlier. We have to infer the cosmic line of events before the CMB using theoretical modeling. Fortunately there are some pieces of evidence today that are relics from the processes that happened during this early stage of the Universe, the most evident being (a) the primordial abundances of the elements and (b) the anisotropies in the CMB and structures that formed in the Universe lateron. We will discuss (b) in Chapter 5. In the present chapter we will discuss the thermal processes that happened in the early Universe and how they created the initial abundances of the elements in our Universe.

7.1 Assumptions

To a surprising degree of accuracy we can assume that the Universe behaves adiabatically, i.e. during the expansion we can assume that all processes are reversible. And it also turns out that we can understand many of the thermal processes in the early universe with thermal equilibrium followed by "freeze-out". What it means is that before that freeze-out time the abundances of species of particles are given by their thermal equilibrium value (which changes with time as the universe cools down), while after that time the abundances stay fixed. This means that we can calculate the abundances to good approximation by finding at which temperature they froze out and taking the thermal equilibrium abundances at that temperature.

This assumption requires that the reactions that convert the different species of particles into each other and/or create/destroy particles are fast enough that at all times before freeze-out the system is in thermal equilibrium. It turns out that this is a reasonable approximation.

So in this chapter we will study the thermal evolution of the early Universe as a series of equilibrium states for all particles that have not yet frozen out.

7.2 A recap of some statistical physics principles

To derive the equilibrium abundances of particles we need some tools from statistical physics. I assume that you are familiar with them, so we will not rigorously derive them from scratch. Some more in-depth discussion can be found in the script on cosmology by Matthias Bartelmann.

7.2.1 Statistical equilibrium of quantum states of identical particles

Suppose we have N identical particles. Each can acquire energy states ϵ_m with $m = 0, 1, 2, 3, \cdots, M$. A point in this phase space can be denoted as $(m_1, m_2, \cdots, m_N)$, meaning that particle 1 is in state m_1 (having energy ϵ_{m_1}), particle 2 is in state m_2 etc. Each phase space point has many "twins": other phase space points that are physically the same. Example: $(1, 0, 0)$ is the same as $(0, 1, 0)$ etc. Let us call each point in phase space a *microstate* and the the total set of identical microstates a *distribution*. A nice way to denote a distribution is to count how many of the N particles are in each one-particle energy state: $\{N_0, N_1, \cdots, N_M\}$, where $\sum_m N_m = N$. Example: The distribution belonging to microstate $(0, 0, 1, 1, 0, 2, 0)$ would be $\{4, 2, 1, 0, 0, \cdots\}$, but also microstate $(1, 1, 0, 0, 0, 2, 0)$ has the same distribution.

A fundamental principle of statistical physics is that all microstates have the same probability, provided some constraint equations are fulfilled. The constraint equations are, in our example, that the total number of particles is a given value (N) and that the total energy also equals a given value (E). The distribution which corresponds to the largest number of identical microstates is therefore the most likely distribution. The result is (without proof):

$$N_m = \frac{N}{Z_1} e^{-\epsilon_m/kT} \tag{7.1}$$

where T is the temperature and k is the Bolztmann constant. The symbol Z_1 is a normalization constant such that $\sum_m N_m = N$ and is called the *partition sum*:

$$Z_1 = \sum_{m=0}^{M} e^{-\epsilon_m/kT} \tag{7.2}$$

Often quantum states are degenerate: they in fact consist of a multitude of states with identical energy ϵ, typically as a result of rotational symmetry of the particle. Rather than treating each of these states separately, we pack them together as a single state m with energy ϵ_m and a degeneracy g_m (also called "statistical weight" g_m). We then get

$$N_m = \frac{N g_m}{Z_1} e^{-\epsilon_m/kT} \tag{7.3}$$

$$Z_1 = \sum_{m=0}^{M} g_m e^{-\epsilon_m/kT} \tag{7.4}$$

Later, when we will allow particles to be created, destroyed and/or transformed into another type of particle (through e.g. chemical reactions), it will be important to include also the *chemical potential* μ to these equations. Without proof this leads to

$$N_m = \frac{N g_m}{Z_1} e^{-(\epsilon_m-\mu)/kT} \tag{7.5}$$

$$Z_1 = \sum_{m=0}^{M} g_m e^{-(\epsilon_m-\mu)/kT} \tag{7.6}$$

Note, however, that for a system of fixed $N = \sum_m N_m$ the inclusion of μ in the above equations does not change anything: μ drops out of Eq. (7.5) and thus Eqs. (7.5,7.6) are equivalent to Eqs. (7.3,7.4).

7.2.2 Maxwell-Boltzmann distribution

If we consider the movement of the N particles, then their "quantum states" are their momenta $\vec{p} = m\vec{v}$ where m is the particle mass (not to be confused with the *index* m for the quantum states). In $(\vec{x}, \vec{p})$-space one quantum unit has volume h^3. Eqs. (7.3,7.4) should then be applied to these quantum units. Since the quantum units of $(\vec{x}, \vec{p})$-space are so small, the sum in Eq. (7.6) can be expressed as an integral:

$$Z_1 = \frac{gV}{h^3} \int e^{-(\epsilon(\vec{p})-\mu)/kT} d^3p = \frac{4\pi gV}{h^3} \int_0^\infty e^{-(\epsilon(p)-\mu)/kT} p^2 dp \tag{7.7}$$

The energy $\epsilon(p)$ is, in the low-velocity-limit of special relativity, expressed as

$$\epsilon(p) = mc^2 + \frac{p^2}{2m} \tag{7.8}$$

So Z_1 becomes

$$\begin{aligned} Z_1 &= \frac{4\pi gV}{h^3} e^{-(mc^2-\mu)/kT} \int_0^\infty e^{-p^2/(2mkT)} p^2 dp \\ &= \frac{gV(2\pi mkT)^{3/2}}{h^3} e^{-(mc^2-\mu)/kT} \end{aligned} \tag{7.9}$$

According to Eq. (7.5) the number of particles N_m per quantum state m is

$$\begin{aligned} N_m &= \frac{Ng}{Z_1} e^{-p^2/(2mkT)} e^{-(mc^2-\mu)/kT} \\ &= \frac{Nh^3}{V(2\pi mkT)^{3/2}} e^{-p^2/(2mkT)} \end{aligned} \tag{7.10}$$

Again: The m in N_m is an index, while the m in the rest is the particle mass.

Now it is convenient to define a one-particle distribution function $f(\vec{p})$ such that $f(\vec{p})d^3p$ describes the chance of finding a given particle in a box of momentum-volume d^3p around momentum vector $\vec{p}$. It therefore holds that $\int f(\vec{p})d^3p = 1$. In a spatial volume V a quantum unit in $\vec{p}$-space has $\Delta p^3 = h^3/V$, and thus $N_m = Nf(\vec{p})h^3/V$. This gives

$$f(\vec{p}) = \frac{1}{(2\pi mkT)^{3/2}} e^{-p^2/(2mkT)} \tag{7.11}$$

If we define $f(p) = 4\pi p^2 f(\vec{p})$ (such that $\int_0^\infty f(p)dp = 1$) we arrive at

$$f(p) = \frac{4\pi}{(2\pi mkT)^{3/2}} p^2 e^{-p^2/(2mkT)} \tag{7.12}$$

This is the Maxwell-Boltzmann distribution.

7.2.3 Chemical reactions in equilibrium

If we have multiple species in the same box, then each of these species has its own chemical potential μ_i. Suppose we have a chemical reaction

$$\alpha_1 \text{Species}_1 + \alpha_2 \text{Species}_2 \leftrightarrow \beta_3 \text{Species}_3 + \beta_4 \text{Species}_4 \tag{7.13}$$

We can define a parameter ξ that determines how far the reaction has proceeded (in the direction from 1,2 to 3,4):

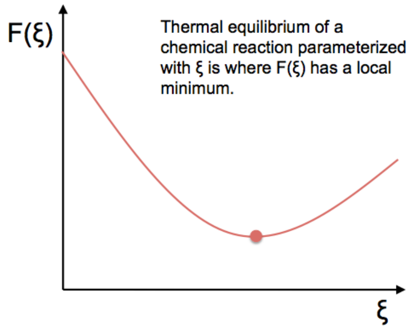
$$\frac{dN_1}{d\xi} = -\alpha_1 \qquad \frac{dN_2}{d\xi} = -\alpha_2 \qquad \frac{dN_3}{d\xi} = \beta_3 \qquad \frac{dN_4}{d\xi} = \beta_4 \tag{7.14}$$

According to the rules of statistical physics (without proof) the equilibrium of this reaction (with constant volume and temperature) is found when

$$\frac{dF(\xi)}{d\xi} = 0 \tag{7.15}$$

where F is the *free energy* of the system (we will come back to this later). Eq. (7.15) says that the system in chemical equilibrium (assuming only the above chemical reaction is possible) when we are at a minimum of F *along the reaction track*. This means that

$$\frac{dF(\xi)}{d\xi} = -\alpha_1 \frac{\partial F}{\partial N_1} - \alpha_2 \frac{\partial F}{\partial N_2} + \beta_3 \frac{\partial F}{\partial N_3} + \beta_4 \frac{\partial F}{\partial N_4} = 0 \tag{7.16}$$



where the notation is such that

$$\frac{\partial F}{\partial N_i} \equiv \left(\frac{\partial F}{\partial N_i}\right)_{N_{j\neq i}=\mathrm{const}} \tag{7.17}$$

If we define the chemical potentials μ_i as

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{N_{j\neq i}=\mathrm{const}} \tag{7.18}$$

then we get

$$-\alpha_1\mu_1 - \alpha_2\mu_2 + \beta_3\mu_3 + \beta_4\mu_4 = 0 \tag{7.19}$$

We can also express dN_2, dN_3 and dN_4 all in terms of dN_1, because we have to move along the chemical reaction:

$$dN_2 = \frac{\alpha_2}{\alpha_1} dN_1 \qquad dN_3 = -\frac{\beta_3}{\alpha_1} dN_1 \qquad dN_4 = -\frac{\beta_4}{\alpha_1} dN_1 \tag{7.20}$$

In that case the $dF(\xi)/d\xi = 0$ condition becomes

$$\frac{dF(N_1)}{dN_1} = 0 \tag{7.21}$$

where it is understood that this is along the reaction path. This way of writing is also often useful, if we know the expression for $F(N_1, N_2, N_3, N_4)$.

It is essential in this theory to understand that the values of N_1, N_2, N_3 and N_4 in equilibrium are found because of their constraint: any increase in N_4 goes along with a decrease in N_1.

There is also a special kind of reaction: Particle creation, like the creation of photons:

$$\alpha_1 \mathrm{Species}_1 + \alpha_2 \mathrm{Species}_1 \leftrightarrow \alpha_1 \mathrm{Species}_1 + \alpha_2 \mathrm{Species}_1 + \beta \mathrm{Species}_1 \tag{7.22}$$

for instance:

$$p + e \leftrightarrow p + e + \gamma \tag{7.23}$$

In this case one could say $\beta_1 = \alpha_1$ and $\beta_2 = \alpha_2$ so the equation $dF(\xi)/d\xi = 0$ becomes

$$-\alpha_1\mu_1 - \alpha_2\mu_2 + \beta_1\mu_1 + \beta_2\mu_2 + \beta_3\mu_3 = \beta_3\mu_3 = 0 \tag{7.24}$$

This means

$$\mu_3 = 0 \tag{7.25}$$

The chemical potential of this particle 3 (in our example this is a photon) must therefore be 0. This is because the number of photons is not constrained by any constraint equation.

We can also do a mixed-form reaction: partly constrained and partly unconstrained. An example is ionization/recombination:

$$p + e \leftrightarrow H + \gamma \tag{7.26}$$

The constraint is

$$dN_p = dN_e \qquad dN_H = -dN_p \tag{7.27}$$

In principle one would also have $dN_\gamma = dN_H$. In that case we would have $\alpha_p = 1$, $\alpha_e = 1, \beta_H = 1$ and $\beta_\gamma = 1$, i.e. $\mu_p + \mu_e = \mu_H + \mu_\gamma$. But often there is no constraint on N_γ, for instance if one is assumed to be in a known radiation field where $N_\gamma \gg N_H$, so that an ionization event does not affect N_γ very much. In that case we keep μ_γ fixed.

$$\mu_p + \mu_e = \mu_H + \mu_\gamma^{(\text{fixed})} \tag{7.28}$$

If, on top of that, the radiation field is thermal, then $\mu_\gamma = 0$, in which case we obtain

$$\mu_p + \mu_e = \mu_H \tag{7.29}$$

7.2.4 Saha equation

Using the above rules we can derive the equilibrium values of N_e, N_p and N_H under the presence of ionization/recombination reactions. Since we want to find the minimum of the free energy F we express F first in terms of the *canonical partition function* Z_c of the combined system of three species (without proof):

$$F = -kT \ln(Z_c) \tag{7.30}$$

with (also without proof; see lectures on statistical physics):

$$Z_c = \frac{Z_e^{N_e} Z_p^{N_p} Z_H^{N_H}}{N_e! N_p! N_H!} \tag{7.31}$$

where Z_e, Z_p and Z_H are the one-particle partition functions for electrons, protons and hydrogen atoms, respectively (cf. Eq. 7.9).

Let us define the baryon number $N_b = N_p + N_H$ which is conserved. The hydrogen density can be expressed in terms of N_b and N_e by $N_H = N_b - N_e$. For the $\ln(N!)$ terms we use Stirling's formula $\ln(N!) = N(\ln N - 1)$. If we take as our reaction parameter $d\xi = dN_e$ we have

$$\frac{dN_e}{d\xi} = 1 \qquad \frac{dN_p}{d\xi} = 1 \qquad \frac{dN_H}{d\xi} = -1 \tag{7.32}$$

We can now express $dF(\xi)/d\xi$ as

$$\begin{aligned} 0 = \frac{dF(\xi)}{d\xi} &= \frac{d}{d\xi}\Big[N_e \ln Z_e + N_p \ln Z_p + N_H \ln Z_H \\ &\quad - N_e(\ln N_e - 1) - N_p(\ln N_p - 1) - N_H(\ln N_H - 1)\Big] \\ &= \ln Z_e + \ln Z_p - \ln Z_H - \ln N_e - \ln N_p + \ln N_H \end{aligned} \tag{7.33}$$

This immediately implies

$$\frac{N_e N_p}{N_H} = \frac{Z_e Z_p}{Z_H} \tag{7.34}$$

With Eq. (7.9), together with $(m_e + m_p - m_H)c^2 = 13.6$ eV and $\mu_e + \mu_p - \mu_H = 0$ and $g_e g_p / g_H = 1$, and the identities $N_e = N_p$ and $N_H = N_B - N_e$ we obtain

$$\frac{N_e^2}{N_b - N_e} = \frac{V(2\pi m_e kT)^{3/2}}{h^3} e^{-\chi/kT} \tag{7.35}$$

with $\chi = 13.6$ eV. Here we used $m_p/m_H \simeq 1$. We can write this with $x = N_e/N_b$ and $n_b = N_b/V$ as

$$\frac{x^2}{1-x} = \frac{(2\pi m_e kT)^{3/2}}{h^3 n_b} e^{-\chi/kT} \tag{7.36}$$

This is Saha's equation for thermal ionization equilibrium.

7.2.5 Equilibrium number densities without constraints

If a particle can be created and destroyed without constraints (other than the energy of course), we have already seen that their chemical potential μ in thermal equilibrium is 0. This is, for instance, the case for photons, but at very high temperatures this might also be approximately the case for other particles. For instance, at very high temperatures you can create e^+e^- pairs in abundance, as much as the available energy allows you. As long as this number is much larger than the pre-existing electrons, the abundance of e^+e^- pairs is nearly unconstrained, and will have a near-zero chemical potential. This leads to a well-defined occupation number of each quantum state (without proof):

$$N_m = \frac{1}{e^{\epsilon/kT} \pm 1} \tag{7.37}$$

where the + is for fermions and the − for bosons.

For photons with $\epsilon = h\nu$ we thus get

$$N_m^{\text{(Planck)}} = \frac{1}{e^{h\nu/kT} - 1} \tag{7.38}$$

Since the density of quantum states (per volume per frequency) is $\rho_s = 4\pi g\nu^2/c^3$ (with $g = 2$ for photons), and the energy per photon is $h\nu$ we see that the equilibrium energy for light $U(\nu)$ is

$$U(\nu) = \frac{4\pi g h\nu^3/c^3}{e^{h\nu/kT} - 1} \tag{7.39}$$

Now, per sterradian (dividing by 4π) and passing through a surface of 1 cm^2 per second (multiplying with c) this gives the Planck function:

$$B_\nu(T) = \frac{2h\nu^3/c^2}{e^{h\nu/kT} - 1} \tag{7.40}$$

where we inserted $g = 2$. This is the intensity of thermal radiation of a given temperature T (blackbody radiation), and it is an extremely good approximation to the intensity of the CMB if we take $T = T_{\text{CMB}} = 2.725$ K.

A similar exercise can be made for fermions such as electron/positron pairs, but we will not do this here.

We can also compute the *total* number of particles of a certain kind in equilibrium, which is $N = \sum_m N_m$. After some algebra (see, if you are interested, the script by Bartelmann) one obtains

$$n_B = g_B \frac{\zeta(3)}{\pi^2} \left(\frac{kT}{\hbar c}\right)^3 \quad , \quad n_F = \frac{3}{4}\frac{g_F}{g_B} n_B \tag{7.41}$$

where $n = N/V$, and F stands for fermion and B for boson. Here $\zeta(3) = 1.202$ is the Riemann Zeta-function evaluated at 3. This gives $n_B \simeq 10.14\, g_B (T/K)^3$ cm^{-3}. Note that this means that for the CMB at the present time, with $T_{\text{CMB}} = 2.725$ K we get about 400 photons per cm^3. Most of these photons are at energies close to the peak of the Planck function.

Likewise we can calculate the total energy U for the particles. The result is:

$$u_B = g_B \frac{\pi^2}{30} \frac{(kT)^4}{(\hbar c)^3} \quad , \quad u_F = \frac{7}{8}\frac{g_F}{g_B} u_B \tag{7.42}$$

where $u = U/V$. For photons this gives an average energy per photon of $\langle h\nu \rangle = 2.7\, kT$.

The total entropy S is

$$s_B = g_B k \frac{2\pi^2}{45} \left(\frac{kT}{\hbar c}\right)^3 \quad , \quad s_F = \frac{7}{8}\frac{g_F}{g_B} s_B \tag{7.43}$$

where $s = S/V$.

7.3 Thermal evolution of the early Universe

7.3.1 Adiabatic expansion of thermal radiation

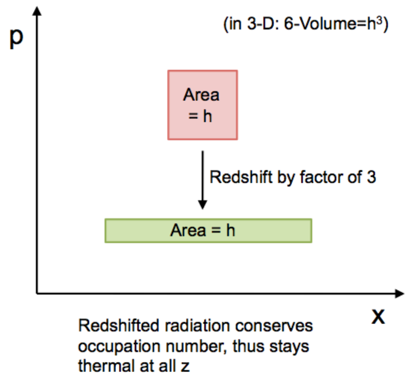
We already saw in Section 4.4 that adiabatic expansion of an isotropic radiation field leads to

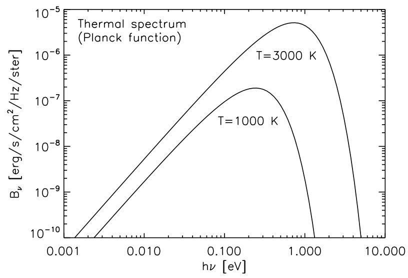
$$\rho \propto p \propto \frac{1}{a^4} \propto \frac{1}{V^{4/3}} \tag{7.44}$$

where the volume $V \propto a^3$. If this radiation field consists of photons in thermal equilibrium, then from Eq. (7.42) we find (with $u_F \equiv \rho$)

$$T \propto \frac{1}{a} \propto \frac{1}{V^{1/3}} \tag{7.45}$$

The temperature thus scales in the same way as the frequency of the photons $\nu \propto 1/a$. This means that if we follow a photon during the expansion of the Universe, the ϵ_m/kT in the expression for the occupation number of quantum states (Eq. 7.37) stays the same. The occupation numbers N_m of the quantum states do not change: Just the energy ϵ_m corresponding to those states goes as $1/a$. This has a very important consequence: *The spectrum of a thermal radiation field remains thermal, even after adiabatic expansion; only the temperature belonging to that thermal radiation field decreases*. This means that the CMB is a thermal spectrum today, both in terms of the spectral shape as well as in terms of the photon density.





7.3.2 Adiabatic expansion of non-relativistic ideal gases

For non-relativistic matter we have already seen that, to first order, $\rho \propto 1/a^3$. However, this tells nothing about the temperature of that matter, since this relation holds in the limit of infinitely cold matter. To find how the temperature of non-relativistic gas behaves we must look at the adiabatic index γ of the gas, defined by

$$p \propto \rho^\gamma \tag{7.46}$$

The γ is related to the number of degrees of freedom n that the particles of the gas have:

$$\gamma = \frac{n+2}{n} \tag{7.47}$$

For point particles one has $n = 3$ because of the x, y and z directions of motion. This gives $\gamma = 5/3$. For a diatomic molecule, for instance, we have two additional degrees of freedom provided by rotation, i.e. for such gas we have $n = 5$ and thus $\gamma = 7/5$. The more degrees of freedom the particles have the more γ approaches 1, i.e. the "softer" the matter becomes. Note that in the notation of Eq. (7.46) radiation would have $\gamma = 4/3$.

For an ideal gas consisting of particles with mass m one has

$$p = \frac{\rho k T}{m} \tag{7.48}$$

This means that as the Universe expands the temperature of this non-relativistic gas goes as

$$T \propto \frac{p}{\rho} \propto \rho^{\gamma-1} \propto a^{3(1-\gamma)} \tag{7.49}$$

For monoatomic gas ($\gamma = 5/3$) we thus have

$$T \propto \frac{1}{a^2} \tag{7.50}$$

This means that non-relativistic gas cools faster than radiation.

7.3.3 Particle freeze-out

Let us verify if the assumption that we have thermal equilibrium at large a followed by freeze-out at smaller z is correct. We do this by setting up a reaction rate equation for the production and destruction of some particle species, which we call s. Let us call the number density of this species n_s. Such a particle can be created by a collision between two other particles, who's number density we write as n_a and n_b. We write the collisional cross section between particle type a and particle type b as σ_{ab}, and we define $p_{ab\rightarrow sc}$ the probability that upon such a collision a particle of type s is formed, including some additional particle c (for momentum and energy conservation). If the average relative velocity between particles a and b is written as $\langle\Delta v_{ab}\rangle$, then the rate of production of particles of type s (and thus also of type c, but that is irrelevant here) is:

$$j_{ab\rightarrow sc} = n_a n_b \langle\Delta v_{ab}\rangle\sigma_{ab}p_{ab\rightarrow sc} \tag{7.51}$$

Now let us assume that a particle of type s can be destroyed again by collisions with some particle of type c with number density n_c (and thus create particles a and b again).

$$j_{sc\rightarrow ab} = n_s n_c \langle\Delta v_{sc}\rangle\sigma_{sc}p_{sc\rightarrow ab} \tag{7.52}$$

You see that $j_{ab\rightarrow sc}$ does not depend on n_s, but $j_{sc\rightarrow ab}$ *does*. Therefore it is convenient to define

$$j \;:=\; j_{ab\rightarrow sc} = n_a n_b \langle\Delta v_{ab}\rangle\sigma_{ab}p_{ab\rightarrow sc} \tag{7.53}$$

$$\alpha \;:=\; j_{sc\rightarrow ab}/n_s = n_c \langle\Delta v_{sc}\rangle\sigma_{sc}p_{sc\rightarrow ab} \tag{7.54}$$

so that neither j nor α depend on n_s. The symbol α is the destruction rate *per particle of type s*. The average life time of these particles is

$$\tau_{\mathrm{life}} = 1/\alpha \tag{7.55}$$

At any redshift z the change in the number density n_s obeys the following equation:

$$\dot{n}_s + 3Hn_s = j - \alpha n_s \tag{7.56}$$

If both $j = 0$ and $\alpha = 0$ (no collisions), then Eq. (7.56) reduces to

$$\dot{n}_s = -3Hn_s \tag{7.57}$$

which implies that $n_s \propto 1/a^3$. This is simply the conservation equation for number density in an expanding Universe.

If both j and α are extremely large, then Eq. (7.56) implies that n_s is given by

$$n_s = \frac{j}{\alpha} \tag{7.58}$$

which is the equilibrium value for n_s. Let us denote this equilibrium value as n_{sT}. We can thus rewrite Eq. (7.56) as

$$\dot{n}_s + 3Hn_s = n_s\alpha\left(\frac{n_{sT}}{n_s} - 1\right) \tag{7.59}$$

If we go back in time to very small a, then α increases rapidly: We have $\alpha \propto n_a n_b \sqrt{T}$, meaning that with $n_a \propto n_b \propto 1/a^3$ and $T \propto 1/a$ (for the radiation era, see Section 7.3.1) we get

$$\alpha \propto \frac{1}{a^{13/2}} \tag{7.60}$$

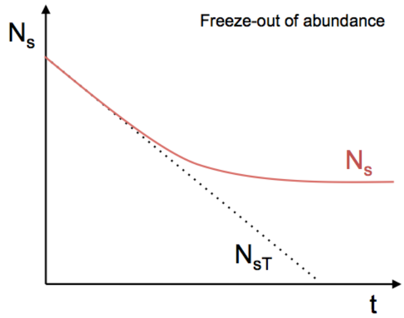
How large must α be to achieve this equilibrium? The trick is to compare $\tau_{\mathrm{life}} = 1/\alpha$ with the Hubble time $1/H$. So if $\alpha \gg H$ then we can expect that n_s is in equilibrium, while if $\alpha \simeq H$ equilibrium is no longer guaranteed and freeze-out sets in. For $\alpha \ll H$ we essentially have no more collisions, and the population has frozen out completely, behaving as $n_s \propto 1/a^3$. With $H \propto 1/a^2$ (cf. Eq. 4.50) we get

$$\frac{\alpha}{H} \propto \frac{1}{a^{9/2}} \tag{7.61}$$

This means that as we go toward smaller a we will inevitably find a point where α/H starts exceeding unity, i.e. where thermal equilibrium is guaranteed. Likewise, for sufficiently large a there will be a point where collisions can be ignored.

If we define

$$N_s = n_s a^3 \qquad \text{and} \qquad N_{sT} = n_{sT} a^3 \tag{7.62}$$



then Eq. (7.59) becomes

$$\frac{d\ln N_s}{dt} = \alpha\left(\frac{N_{sT}}{N_s} - 1\right) \tag{7.63}$$

With $Hdt = d\ln a$ we get

$$\frac{d\ln N_s}{d\ln a} = \frac{\alpha}{H}\left(\frac{N_{sT}}{N_s} - 1\right) \tag{7.64}$$

Here again you clearly see the importance of the α/H ratio in determining whether N_s is always forced to be close to N_{sT} or not. If N_{sT} does not change with a, then once $N_s \simeq N_{sT}$, this will stay like that even after $\alpha/H \ll 1$.

If $N_{sT}(t)$ changes with time, then $N_s(t)$ will follow $N_{sT}(t)$ as long as $\alpha/H \gg 1$. Once $\alpha/H \lesssim 1$ the value of $N_s(t)$ will flatten-off. This is called "freeze-out".

As we have seen in Sections 7.3.1 and 7.2.5, radiation has $n \propto 1/a^3$, i.e. for radiation particles we would have $N_{sT}(t)$ =constant. This means that radiation does not really "freeze out" because even after it is thermally decoupled from the rest of the matter, N_s stays at the thermal value N_{sT} automatically. This is one of the reasons why the CMB is so extremely close to a perfect blackbody spectrum, as we shall see later.

There is also another type of "freeze-out" that we will often encounter: even if the reaction timescales are still much smaller than the expansion timescale, the temperature may drop below the threshold for the reaction. This meanins that the reaction will then, in equilibrium, quickly go in one direction: toward the lower energy state. Under the conditions we will encounter, where the baryons are emersed in a sea of photons with much higher number density, this "shut off" can be a quite steep function of temperature and thus happen rather abruptly.

7.4 Thermal events from 0.1 second until recombination

Now finally we have all the tools in place to study the formation of the elements in the early Universe, effects such as the production of the cosmic neutrino background and, finally, the recombination of the Universe and the release of the CMB. But before doing that we must estimate the number density of baryons.

7.4.1 Baryon to photon ratio

In the very early Universe ($\ll 10^{-12}$ seconds after the Big Bang) there was some, as yet not well understood, mechanism that produced an asymmetry in the number of Baryons over anti-Baryons. This asymmetry was small:

$$\frac{n'_b - n'_{\bar{b}}}{n'_b} \sim 10^{-9} \tag{7.65}$$

where n'_b and $n'_{\bar{b}}$ are the number densities of baryons and anti-baryons at this early time. But without this asymmetry the Universe today would not have contained any atoms. It is currently a major field of research in theoretical physics to explain this asymmetry. The CP-violation (violation of the supposed symmetry of charge and parity of particles) discovered experimentally in the 60s may have something to do with it, but the jury is still out.

At some point the Universe had cooled down enough that all baryon-anti-baryon pairs annihilated, leaving the excess of baryons as the only surviving baryonic matter:

$$n_b = n'_b - n'_{\bar{b}} \tag{7.66}$$

Today we can observationally determine n_b, but can we know what the original n'_b and $n'_{\bar{b}}$ were, i.e. how big the asymmetry was? In thermal equilibrium the number of baryons $n'_b \simeq n'_{\bar{b}}$ must have been comparable to the photon density n'_γ according to Eq. (7.41). It therefore gives an estimate of the asymmetry to compare n_b to the number of photons n_γ from the CMB today:

$$\eta := \frac{n_b}{n_\gamma} \tag{7.67}$$

Both n_b and n_γ scale as $1/a^3$ as we know from Sections 7.3.1 and 7.3.2, that is: as long as the total particle number does not change. For the baryons that number has not changed since the annihilation of baryons and anti-baryons. For the photons of the CMB that number has last changed around 1 second after the Big Bang (see Section 7.4.2). So if we measure η today, it is valid back to 1 second after the Big Bang.

As we shall see later, the baryon density $\Omega_{b,0}$ can be estimated from the anisotropies of the CMB. Its value is, according to the latest WMAP results: $\Omega_{b,0} = 0.0456$ (see Table 4.1), which at the present time, with m_b the proton mass $m_b = m_p = 1.67\times10^{-24}$ gram leads to

$$n_b = \frac{\Omega_{b,0}\rho_{\text{crit},0}}{m_p} = \simeq 2.5\times10^{-7}\ (\text{p},\text{n})/\text{cm}^3 \tag{7.68}$$

The number density of photons today is by far dominated by the CMB, for which we know the temperature exactly $T_{\text{CMB}} = 2.725\,\text{K}$. With Eq. (7.41) gives

$$n_\gamma = 10.14 g_\gamma (T/K)^3 = 410\ \text{photons/cm}^3 \tag{7.69}$$

This gives

$$\eta = 6\times10^{-10} \tag{7.70}$$

This shows (a) how small the baryon-anti-baryon asymmetry was and (b) that for every baryon in the Universe there are over 1 billion photons! The latter fact plays an important role in what follows. Another important consequence is that the entropy of the Universe is dominated by a huge margin by the CMB photons.

7.4.2 Neutrino background and electron-positron sea

Around 0.1 seconds after the Big Bang the Universe was filled with electron-positron pairs, neutrino-antineutrino pairs and photons, all with their thermal equilibrium abundances. As we saw in Section 7.4.1 there were also neutrons and protons, but their number densities and total energy density were extremely low compared to those of the neutrinos, electron/positrons and photons. The density of the Universe was so large that neutrinos were routinely absorbed and re-created through the weak interaction:

$$\nu + \bar{\nu} \leftrightarrow e^+ + e^- \tag{7.71}$$

At temperatures of about $10^{10.5}$ K these interactions froze out and the neutrino background was released. It should still be with us today, but it is extremely hard to detect, so we have no proof of its existence yet.

After the freeze-out of the weak interaction, the sea of e^+, e^- was kept at thermal equilibrium through

$$\gamma + \gamma \leftrightarrow e^+ + e^- \tag{7.72}$$

As the Universe cooled down, however, there inevitably comes a time when the average photon energy $\langle h\nu \rangle = 2.7kT$ drops below the rest mass energy $m_e c^2$ of an electron, which happens at

$$T \simeq \frac{m_e c^2}{2.7k} = 2.2 \times 10^9\,\mathrm{K} \tag{7.73}$$

After that time the forward direction of reaction Eq. (7.72) becomes more and more difficult and very rapidly all e^+, e^- pairs annihilate through

$$e^+ + e^- \rightarrow \gamma + \gamma \tag{7.74}$$

Before this happened the temperatures of the photon sea and the neutrino sea remain the same, as they both cool in the same way (cf. Section 7.3.1). However, when the electron-positron pairs suddenly vanish, the energy that was initially in *both* the pairs and the photons suddenly has to be accounted for by *only* the photons. The temperature scaling of Section 7.3.1 was valid if the number of particles (photons in this case) remains constant in time, or more properly formulated: if the entropy of the photon gas stays the same. However, reaction Eq. (7.74) shows that the electrons give all their energy (entropy) to the photons. Once this process was finished the photons had substantially more entropy than before, and thus would have been hotter than Section 7.3.1 predicted. During the pair annihilation phase the temperature of the photon gas therefore decreased only very slowly, as the adiabatic cooling was continuously compensated by $\gamma + \gamma$ productions.

If we write the entropies of e^+, e^- and γ before the annihilation phase as s'_{e^+}, s'_{e^-} and s'_γ and the entropy of the γ after the annihilation phase as s_γ then the transfer of entropy from the pairs to the photons can be written as

$$s'_{e^+} + s'_{e^-} + s'_\gamma = s_\gamma \tag{7.75}$$

The statistical weights of all three particles is 2: $g_{e^+} = g_{e^-} = g_\gamma = 2$. With these statistical weights we can use the formulae from Section 7.2.5 to infer that

$$s'_{e^+} = s'_{e^-} = \frac{7}{8} s'_\gamma \tag{7.76}$$

Eq. (7.75) then becomes

$$\left(\frac{7}{8} + \frac{7}{8} + 1\right) s'_\gamma = \frac{11}{4} s'_\gamma = s_\gamma \tag{7.77}$$

Since $s_\gamma \propto T^3$ we get

$$T_\gamma = \left(\frac{11}{4}\right)^{1/3} T'_\gamma \simeq 1.4 T'_\gamma \tag{7.78}$$

meaning that the photon gas after annihilation is hotter by a factor of 1.4 compared to the case if no annihilation would have taken place. Since the neutrinos have not experienced any of this, we must infer that

$$T_\gamma \simeq 1.4 T_\nu \tag{7.79}$$

This is still so today, so that we expect the cosmic neutrino background temperature to be around 1.95 K. The energy density of the neutrino background is about 1/4 that of the CMB, as can be derived from Eq. (7.42). In these derivations we have, however, assumed that the neutrinos all have neglible masses. If the neutrino masses are non-neglible they may have cooled down much further than this.

7.4.3 Freeze-out of neutron-proton ratio

While the baryon number density is fixed by the baryon-anti-baryon asymmetry, their identity (whether they are neutron or proton) around the time of neutrino freeze-out is not yet determined. This is because of weak interactions such as

$$n + \nu_e \leftrightarrow p + e^- \tag{7.80}$$

Well before the annihilation of the positrons the number density of electrons is very much higher than the number of protons, and so is the number of neutrinos. Both populations have thermal number densities and hence zero chemical potential. That means that reaction Eq. (7.80) does not appreciably affect the number densities of neutrinos and electrons, so that in this reaction they are unconstrained. Only the number of protons and neutrons are constrained. Their thermal abundance ratio is therefore

$$\frac{n_n}{n_p} = e^{-\Delta mc^2/kT} \tag{7.81}$$

where $\Delta m = 1.4\,\mathrm{MeV}$ is the mass difference between a neutron and a proton. Reaction Eq. (7.80) freezes out at temperatures around 800 keV $\simeq 9 \times 10^9\,\mathrm{K}$. This gives a neutron-proton ratio of about

$$\frac{n_n}{n_p} \simeq \frac{1}{6} \tag{7.82}$$

at the time of freeze-out.

7.4.4 Formation of deuterium

Around 3 minutes after the Big Bang, the temperature has dropped to about 80 keV $\simeq 9\times10^8\,\mathrm{K}$ which is low enough for neutrons and protons to fuse and form deuterium. By this time about 20% of the neutrons have already spontaneously decayed through the process:

$$n \to p + e^- + \nu_e \tag{7.83}$$

because the half-life of neutrons is 887 seconds $\simeq$ 15 minutes. So by the time fusion starts we have

$$\frac{n_n}{n_p} \simeq \frac{1}{7} \tag{7.84}$$

The fusion of n and p is given by the reaction

$$n + p \leftrightarrow D + \gamma \tag{7.85}$$

This reaction does not entirely proceed in equilibrium (see later), but one can use equilibrium theory to get a feeling for the temperature at which deuterium can form. We use the method used to derive the Saha equation for ionization of Hydrogen (Section 7.2.4). Compared to that section we replace e with n and H with D and we arrive at

$$\frac{N_n N_p}{N_D} = \frac{Z_n Z_p}{Z_D} = \frac{V(2\pi m_n m_p kT)^{3/2}}{m_D^{3/2} h^3} e^{-\chi/kT} \tag{7.86}$$

with $\chi \simeq 2\,\mathrm{MeV}$ being the binding energy of deuterium. If we write $x = N_n/N_n^0 = N_n/(N_n + N_D)$, we can replace (using $N_n^0/N_p^0 = 1/7$, see Eq. 7.84): $N_D = N_n^0(1-x)$, $N_p = N_n^0(x+6)$ and we get

$$\frac{x(x+6)}{1-x} = \frac{(2\pi m_n m_p kT)^{3/2}}{m_D^{3/2} h^3 n_n^0} e^{-\chi/kT} \tag{7.87}$$

with $n_n^0 = N_n^0/V$ the initial neutron number density before deuterium formation. Now, $n_n^0 = n_b/8$ where n_b is the baryon number density. We know from Section 7.4.1 that

$n_b = \eta n_\gamma$ with $\eta = 6\times 10^{-10}$. We also know that the photons are in thermal equilibrium so that with Eq. (7.41) we have $n_\gamma = 2(\zeta(3)/\pi^2\hbar^3c^3)(kT)^3$ This means that we get

$$\frac{x(x+6)}{1-x} = \frac{1}{\eta}\frac{(m_n m_p c^2)^{3/2}}{\zeta(3)\pi(2\pi m_D kT)^{3/2}} e^{-\chi/kT} \tag{7.88}$$

$x = 1$ means no deuterium has formed while $x = 0$ means that all neutrons have been consumed to form deuterium. Eq. (7.88) contains a factor $1/\eta \gg 1$. This means that order for x to become appreciably smaller than 1 the factor χ/kT in the exponent must be very large. Or in other words: the production of deuterium happens at a temperature $kT \ll \chi$. Naively one would expect that this happens around $kT \simeq \chi \simeq 2$ MeV. But because there are so many photons around that can destroy deuterium, the formation of deuterium happens only much later at $kT \simeq 80$ keV.

7.4.5 Formation of helium and lithium

The formation of deuterium is essential for the formation of higher mass elements. In order to form elements such as ^{3}He and ^{4}He directly out of neutrons and protons one would require 3-body or 4-body collisions to happen. The probabilities for such reactions are so low that they can be considered zero. With deuterium present, further elements can be formed through reactions such as:

$$\mathrm{D} + \mathrm{D} \leftrightarrow {}^3\mathrm{He} + n \tag{7.89}$$
$${}^3\mathrm{He} + \mathrm{D} \leftrightarrow {}^4\mathrm{He} + p \tag{7.90}$$
$$\mathrm{D} + n \leftrightarrow \mathrm{T} + \gamma \tag{7.91}$$
$$\mathrm{T} + p \leftrightarrow {}^4\mathrm{He} + \gamma \tag{7.92}$$

where T denotes tritium (^{3}H). This means that it must be possible to form deuterium quickly enough, and deuterium must be long-lived enough, otherwise the Universe would not contain any elements other than hydrogen. If, however, the formation of deuterium would be *too efficient*, then all deuterium would have reacted further to helium, so today there would be no deuterium left. This leads to the Gamov condition, that

$$\langle n_p v\sigma\rangle t \simeq 1 \tag{7.93}$$

where v is the typical velocity of neutrons and protons, σ is the reaction cross section for the formation of deuterium, n_p is the proton number density and t the time scale of nucleosynthesis.

In the end, most of the neutrons end up in ^{4}He. It is, however, not easy to form higher mass elements. The reaction

$$\mathrm{T} +^4 \mathrm{He} \leftrightarrow^7 \mathrm{Li} + \gamma \tag{7.94}$$

causes the formation of Lithium in a tiny amount. Also trace amounts of Beryllium is formed, which is, however, unstable and decays. The main barrier to forming larger mass elements is the absense of stable nuclei of atomic weights 5 and 8. It is therefore not possible to produce a larger mass nucleus from ^{4}He by capturing a neutron or proton, and likewise for ^{7}Li. This means that beyond ^{7}Li essentially no elements are formed. All the heavier elements in the Universe today have been formed in stars.

Since most of the neutrons end up in ^{4}He we can estimate the helium abundance straight from the $n/p = 1/7$ ratio:

$$\begin{aligned} Y &= \frac{m_{He}n_{He}}{m_{He}n_{He} + m_H n_H} = \frac{4(n_n/2)}{4(n_n/2) + (n_p - n_n)} = \frac{2n_n}{n_n + n_p} \\ &= \frac{2(n_n/n_p)}{1 + (n_n/n_p)} = \frac{1}{4} \end{aligned} \tag{7.95}$$

This is a rather robust prediction, and fortunately this is indeed very close to what is observed!

7.4.6 Observational constraints from nucleosynthesis

The primordial abundances are not easy to measure, because most of the matter in the Universe has already been processed into further elements by stellar nucleosynthesis. Therefore one must either observe high redshift objects or find ultra-low metallicity stars in our own Galaxy. But even then it is not easy, because, for instance, deuterium is electronically identical to hydrogen. If deuterium is in the form of a molecule such as DH, then the ro-vibrational spectrum has its lines shifted compared to H_2 because of the intertia of D. Also a tiny shift in the location of the Ly-α line in neutral atomic deuterium can be observed. Likewise the abundance of ^{3}He is not easy to determine, but can be detected via the hyperfine transition of ^{3}He$^+$. However, ^{3}He is not a very reliable tracer because it can be created in pre-main-sequence stars and destroyed in stellar interiors. ^{4}He is easier to detect: via optical recombination lines in HII regions. ^{7}Li can be found in extremely metal-poor star in the galactic halo.

In the lecture, some examples will be shown.

7.4.7 Recombination of the Universe and the release of the CMB

The CMB is released when the electrons, which scatter the radiation and thus make the Universe opaque, recombine with the available ions, or in other words, when the reaction

$$e^- + p \leftrightarrow H + \gamma \tag{7.96}$$

freezes out. This happens when the temperature of the Universe drops well below the ionization energy. Like with the $n + p \leftrightarrow D + \gamma$ reaction in Section 7.4.4 this is a delayed recombination: it happens at a temperature of about 3500 K = 0.3 eV, which is substantially lower than the ionization energy of hydrogen (13.7 eV). The reason is, again, the tiny baron-to-photon ratio η. The Saha equation (Eq. 7.36) can be written, with $n_b = \eta n_\gamma$ as

$$\frac{x^2}{1-x} = \frac{(2\pi m_e kT)^{3/2}}{h^3 \eta n_\gamma} e^{-\chi/kT} \tag{7.97}$$

with $\chi = 13.7$ eV. With $n_\gamma = 2(\zeta(3)/\pi^2\hbar^3c^3)(kT)^3$ (cf. Eq. 7.41) this becomes

$$\frac{x^2}{1-x} = \frac{\sqrt{\pi}}{4\sqrt{2}\zeta(3)\eta}\left(\frac{m_e c^2}{kT}\right)^{3/2} e^{-\chi/kT} \simeq \frac{0.26}{\eta}\left(\frac{m_e c^2}{kT}\right)^{3/2} e^{-\chi/kT} \tag{7.98}$$

Like with the deuterium production, the huge factor $1/\eta$ means that in order to get recombination ($x \to 0$) the factor χ/kT must be $\gg 1$, delaying recombination until 3500 K.

Also, like with the deuterium production, the assumption of strict thermal equilibrium at all times is here a bit too simple. One problem is, for instance, the Ly-α transition at 10.2 eV. It is the ^{2}P$\leftrightarrow$^{2}S electronic transition from the first excited state to the ground state. While such photons cannot directly ionize other hydrogen atoms, they will keep many atoms in a highly excited state (just 3.5 eV below the ionization threshold), making it very easy to reionize them. Moreover, Ly-α photons cannot escape: any photon that is emitted by one hydrogen atom will be reabsorbed by a nearby H atom in the ground state, as long as they are around.This leads to Ly-α *resonant scattering*: When a hydrogen atom absorbs a Ly-α photon it stays excited until it deexcites by sending out a Ly-α photon, which moves a little distance before it gets absorbed again. This process keeps going on as long as there is no mechanism to deexcite the ^{2}P and ^{2}S states of hydrogen in another way. One way would be through a collision with another hydrogen atom, but this rate of collisional de-excitation is rather low. Another way would be by two-photon deexcitation, which is a quadrupole transition and thus "highly forbidden", meaning that its rate is very low compared to "normal" electronic transitions - but still higher than collisional de-excitation at the conditions in the Universe around 3500 K. Since this quadrupole process produces two photons, the energetic constraint is $h\nu_1 + h\nu_2 = 10.2$ eV. This gives a *continuum* of photons that are less energetic than Ly-α. These photons do *not* excite other atoms, meaning that the Ly-α scattering process ends and one atom is now recombined "for real". The low rate of quadrupole emission means that recombination is delayed again a bit.

The recombination process eliminates free electrons and thus eliminates the Thompson scattering opacity of the gas. Neutral hydrogen+helium gas is almost perfectly transparent for optical radiation. This means that the radiation is now set free: the CMB is born. The point of release is rather abrupt, but not infinitely abrupt. There is a certain width in time where the Universe goes from completely opaque to the time when a photon scatters for the last time (the "last scattering surface"). The optical depth through this surface to Thompson scattering is given by

$$\tau = \int n_e \sigma_T dr = n_B \sigma_T \int x dr \tag{7.99}$$

with $\sigma_T = 6.65 \times 10^{-25}$ cm^2 the Thompson cross section and $dr = cdt = cda/\dot{a}$. The chance that a photon scatters for the last time between z and $z + dz$ is

$$p(z)dz = e^{-\tau} d\tau = e^{-\tau} \frac{d\tau}{dz} dz \tag{7.100}$$

It turns out that a reasonably good description of $p(z)$ is

$$p(z) \simeq \frac{1}{\sqrt{2\pi}\sigma_{\rm rec}} \exp\left(-\frac{(z - z_{\rm rec})^2}{2\sigma_{\rm rec}^2}\right) \tag{7.101}$$

with $z_{\rm rec} = 1100$ and $\sigma_{\rm rec} = 80$. This means that the last scatterings happen over a time range during which the temperature drops by roughly 200 K (with 3500 K average).

This does *not* mean that the CMB has a temperature uncertainty of $(200/3500) * 2.725 = 0.156$ K, because the temperature of the free photons scales the same as those of the trapped photons. Note that although we are by now in the matter-dominated era, the energy of matter is dominated by its rest mass, so that the *thermal* energy is still dominated by the radiation field, which means that the temperature scaling is $T \sim 1/a$, meaning that we obtain a CMB of a *single* temperature even though the light is emitted over a range of temperatures.

Once the CMB radiation is set free, the radiation can no longer influence the baryon temperature. Before the release of the CMB the baryon temperature was always kept at the radiation temperature, thus also going as $T \propto 1/a$. But after the CMB release the baryons cool as a monoatomic gas: $T \propto 1/a^2$.