Thermal Equilibrium

The blackbody spectrum of the CMB is strong observational evidence that the early universe was in a state of thermal equilibrium. Moreover, on theoretical grounds, we expect the interactions of the Standard Model to have established thermal equilibrium at temperatures above 100 GeV.

We will describe this initial state of the hot Big Bang and its subsequent evolution using the methods of thermodynamics and statistical mechanics, suitably generalized to apply to an expanding universe.

Some Statistical Mechanics

The early universe was a hot gas of weakly interacting particles. It is impractical to describe this gas by the positions and velocities of each particle. Instead, we will use a coarse-grained description of the gas using the principles of statistical mechanics. In other words, rather than following the evolution of each individual particle, we will characterize the properties of the gas statistically.

Distribution functions

A key concept in statistical mechanics is the probability that a particle chosen at random has a momentum $\mathbf{p}$. In general, this (probability) distribution function, $f(\mathbf{p}, t)$, can be very complicated.[4] However, if we wait long enough (relative to the typical interaction timescale), then the system will reach *equilibrium* and is characterized by a time-independent distribution function. At this point, the gas has reached a state of maximum entropy in which the distribution function is given by either the **Fermi-Dirac distribution** (for fermions) or the **Bose-Einstein distribution** (for bosons)

$$\boxed{f(p,T) = \frac{1}{e^{(E(p)-\mu)/T} \pm 1}} \,,$$

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

The function has two parameters: the temperature, T , and the chemical potential, μ. The latter describes the response of a system to a change in particle numbers. The chemical potential may be temperature dependent, and since the temperature changes in an expanding universe, even the equilibrium distribution functions depend implicitly on time.

Density of states

If a particle has g internal degrees of freedom (for example, due to the intrinsic spin of elementary particles), then the density of states becomes

$$\frac{g}{h^3} = \frac{g}{(2\pi)^3} \,,$$

where in the second equality we have used natural units with $\hbar = h/(2\pi) \equiv 1$.

Densities and pressure

Weighting each state by its probability distribution, and integrating over momentum, we obtain the number density of particles

$$n(T) = \frac{g}{(2\pi)^3}\int \mathrm{d}^3p\, f(p,T)\,.$$

Moreover, the energy density and pressure of the gas are then given by the following integrals

$$\rho(T) = \frac{g}{(2\pi)^3}\int \mathrm{d}^3p\, f(p,T)\,E(p)\,,$$
$$P(T) = \frac{g}{(2\pi)^3}\int \mathrm{d}^3p\, f(p,T)\,\frac{p^2}{3E(p)}\,,$$

where $E(p) = \sqrt{m^2+p^2}$,

Each particle species i (with possibly distinct m_i, μ_i, T_i) has its own distribution function f_i and hence its own density and pressure, n_i, ρ_i, P_i. Species that are in thermal equilibrium share a common temperature, $T_i = T$. Their densities and pressures can then only differ because of differences in their masses and chemical potentials.

At early times, the chemical potentials of all particles are much smaller than the temperature, μi << T , and can hence be neglected. For electrons and protons this is a provable fact, for photons it holds by definition, and for neutrinos it is likely true, but not proven. We will drop the chemical potential from our discussion for now, but return to it later.

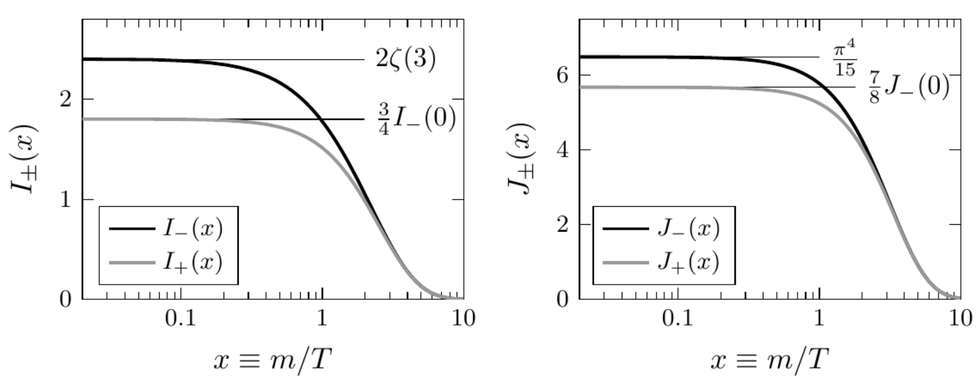
Setting the chemical potential to zero, we get

$$n = \frac{g}{2\pi^2}\int_0^\infty \mathrm{d}p\,\frac{p^2}{\exp\left[\sqrt{p^2+m^2}/T\right]\pm 1}\,,$$
$$\rho = \frac{g}{2\pi^2}\int_0^\infty \mathrm{d}p\,\frac{p^2\sqrt{p^2+m^2}}{\exp\left[\sqrt{p^2+m^2}/T\right]\pm 1}\,.$$

Defining the dimensionless variables $x \equiv m/T$ and $\xi \equiv p/T$, this can be written as

$$n = \frac{g}{2\pi^2}T^3\,I_\pm(x)\,,\qquad I_\pm(x) \equiv \int_0^\infty \mathrm{d}\xi\,\frac{\xi^2}{\exp\left[\sqrt{\xi^2+x^2}\right]\pm 1}\,,$$
$$\rho = \frac{g}{2\pi^2}T^4\,J_\pm(x)\,,\qquad J_\pm(x) \equiv \int_0^\infty \mathrm{d}\xi\,\frac{\xi^2\sqrt{\xi^2+x^2}}{\exp\left[\sqrt{\xi^2+x^2}\right]\pm 1}\,.$$

In general, the functions $I_\pm(x)$ and $J_\pm(x)$ have to be evaluated numerically However, in the relativistic and non-relativistic limits, we can determine them analytically.



Numerical evaluation of the functions $I_\pm(x)$ and $J_\pm(x)$

Relativistic limit

$$\boxed{n = \frac{\zeta(3)}{\pi^2}\, gT^3 \begin{cases} 1 & \text{bosons} \\ \frac{3}{4} & \text{fermions} \end{cases}} \; . \qquad \boxed{\rho = \frac{\pi^2}{30}\, gT^4 \begin{cases} 1 & \text{bosons} \\ \frac{7}{8} & \text{fermions} \end{cases}}$$

Using the observed temperature of the CMB, $T_0 \approx 2.73$ K, we find that the number density and energy density of relic photons today are

$$n_{\gamma,0} = \frac{2\zeta(3)}{\pi^2}\, T_0^3 \approx 410 \text{ photons cm}^{-3} \, ,$$

$$\rho_{\gamma,0} = \frac{\pi^2}{15}\, T_0^4 \approx 4.6 \times 10^{-34} \text{g cm}^{-3} \, .$$

Finally, taking $p = E$ we get

$$P = \frac{1}{3}\rho \, ,$$

as expected for a gas of relativistic particles (“radiation”).

Non-relativistic limit

$$I_{\pm}(x) = \sqrt{\frac{\pi}{2}}\, x^{3/2}\, e^{-x} \, ,$$

$$\boxed{n = g\left(\frac{mT}{2\pi}\right)^{3/2} e^{-m/T}} \; .$$

To determine the energy density in the non-relativistic limit, we write $E(p) = \sqrt{m^2 + p^2} \approx m + p^2/2m$. The energy density then is

$$\rho \approx mn + \frac{3}{2} nT \, ,$$

where the leading term is simply equal to the mass density

Finally, it is easy to show that the pressure of a non-relativistic gas of particles is

$$P = nT \, ,$$

which is nothing but the ideal gas law, $PV = Nk_{\mathrm{B}}T$ (for $k_{\mathrm{B}} \equiv 1$). Since $T \ll m$, we have $P \ll \rho$, so that the gas acts like pressureless dust (“matter”).

The early universe was a collection of different species and the total energy density ρ is the sum over all contributions

$$\rho = \sum_i \frac{g_i}{2\pi^2} T_i^4 J_\pm(x_i)\,,$$

where we have allowed for the possibility that the different species have different temperatures T_i. For the Standard Model, this complication is only relevant for neutrinos after electron-positron annihilation (see Section 3.1.4). It is common to write the density in terms of the "temperature of the universe" T (typically chosen to be the photon temperature T_γ),

$$\rho = \frac{\pi^2}{30} g_*(T) T^4\,,$$

where we have defined the "effective number of degrees of freedom" at the temperature T as

$$g_*(T) \;\equiv \sum_{i=b} g_i \left(\frac{T_i}{T}\right)^4 + \frac{7}{8}\sum_{i=f} g_i \left(\frac{T_i}{T}\right)^4 .$$

When all particles are in equilibrium at a common temperature T, determining $g_*(T)$ is simply a counting exercise.

Table 3.2 Particle content of the Standard Model.

type		mass	spin	g
gauge bosons	γ	0		2
	$W^\pm$	80 GeV	1	3
	Z	91 GeV		
gluons	g_i	0	1	$8 \times 2 = 16$
Higgs boson	H	125 GeV	0	1
quarks	$t, \bar{t}$	173 GeV	$\frac{1}{2}$	$2 \times 3 \times 2 = 12$
	$b, \bar{b}$	4 GeV		
	$c, \bar{c}$	1 GeV		
	$s, \bar{s}$	100 MeV		
	$d, \bar{s}$	5 MeV		
	$u, \bar{u}$	2 MeV		
leptons	$\tau^\pm$	1777 MeV	$\frac{1}{2}$	$2 \times 2 = 4$
	$\mu^\pm$	106 MeV		
	$e^\pm$	511 keV		
	$\nu_\tau, \bar{\nu}_\tau$	< 0.6 eV	$\frac{1}{2}$	$2 \times 1 = 2$
	$\nu_\mu, \bar{\nu}_\mu$	< 0.6 eV		
	$\nu_e, \bar{\nu}_e$	< 0.6 eV		

a massive particle of spin s has $g = 2s + 1$ polarization states.

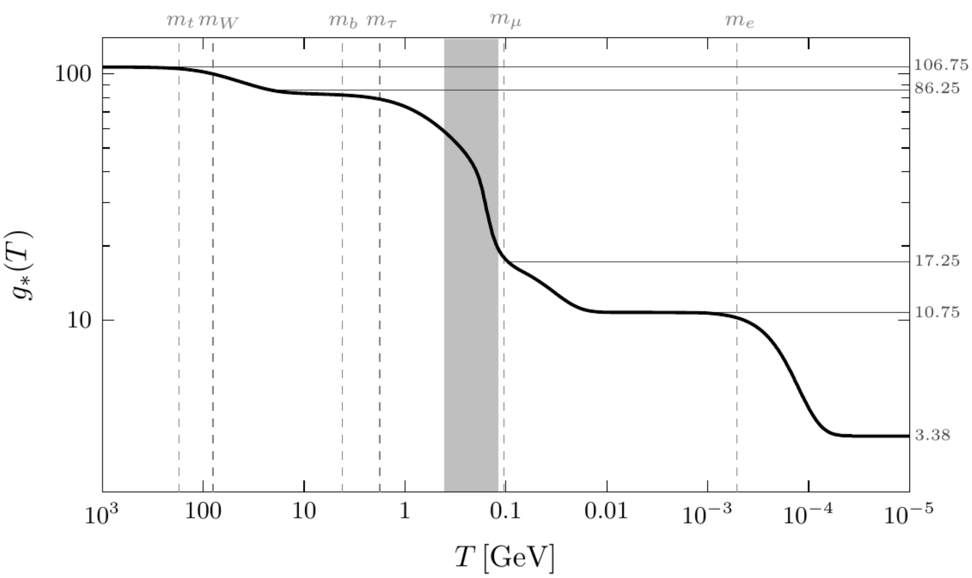
Adding up the internal degrees of freedom, we get

$$g_b = 28 \qquad \text{photons}\,(2),\ W^{\pm} \text{ and } Z\,(3\times 3),\ \text{gluons}\,(8\times 2),\ \text{and Higgs}\,(1)$$
$$g_f = 90 \qquad \text{quarks}\,(6\times 12),\ \text{charged leptons}\,(3\times 4),\ \text{and neutrinos}\,(3\times 2)$$

and hence

$$g_* = g_b + \frac{7}{8} g_f = 106.75\,. \tag{3.38}$$

As the temperature drops, various particle species become non-relativistic and annihilate. This leads to the evolution of $g_*(T)$ shown in Fig. 3.2. To estimate g_* at a temperature T, we simply add up the contributions from all relativistic degrees of freedom (with $m \ll T$) and discard the rest.



Evolution of effective number of relativistic degrees of freedom assuming the Standard Model particle content. The gray band indicates the QCD phase transition.

Entropy and Expansion History

To describe the evolution of the universe it is useful to track a conserved quantity. As we will see, **entropy** is more informative than energy. According to the second law of thermodynamics, the total entropy of the universe only increases or stays constant. As we will now show, entropy is conserved in equilibrium.

Conservation of entropy

In statistical mechanics, a precise definition of entropy can be given in terms of the microstates of the system. Here, we will instead determine the entropy of the primordial plasma from the first law of thermodynamics.

The first law states that the change in the entropy (S) of a system is related to changes in its internal energy (U) and volume (V) as

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V\,,$$

where we have assumed that any chemical potentials are small. Defining the **entropy density** as $s \equiv S/V$, we can write

$$\begin{aligned} T\,\mathrm{d}(sV) &= \mathrm{d}(\rho V) + P\,\mathrm{d}V \\ Ts\,\mathrm{d}V + TV\,\mathrm{d}s &= \rho\,\mathrm{d}V + V\,\mathrm{d}\rho + P\,\mathrm{d}V\,. \end{aligned}$$

Since s and ρ depend only on the temperature T, and not on the volume V, this implies

$$\Big(Ts - \rho - P\Big)\,\mathrm{d}V + V\left(T\,\frac{ds}{dT} - \frac{d\rho}{dT}\right)\mathrm{d}T = 0\,.$$

In order for this to be satisfied for arbitrary variations $\mathrm{d}V$ and $\mathrm{d}T$, the two brackets have to vanish separately: The vanishing of the first bracket implies that the entropy density can be written as

$$\boxed{s = \frac{\rho + P}{T}}\,,$$

while the vanishing of the second bracket enforces that

$$\frac{ds}{dT} = \frac{1}{T}\frac{d\rho}{dT}\,.$$

Using the continuity equation, $d\rho/dt = -3H(\rho + P) = -3H\,Ts$, the last equation can also be written in the following instructive form

$$\frac{d(sa^3)}{dt} = 0\,.$$

This means that the total entropy is conserved in equilibrium and that the entropy density evolves as $s \propto a^{-3}$. This conservation law will be very useful for describing the expansion history of the universe.

For a collection of different species, the total entropy density is

$$s = \sum_i \frac{\rho_i + P_i}{T_i} \equiv \frac{2\pi^2}{45} g_{*S}(T) T^3 \,,$$

where we have defined $g_{*S}(T)$ as the "effective number of degrees of freedom in entropy." Away from mass thresholds, we have

$$g_{*S}(T) \approx \sum_{i=b} g_i \left(\frac{T_i}{T}\right)^3 + \frac{7}{8} \sum_{i=f} g_i \left(\frac{T_i}{T}\right)^3 .$$

When all species are in equilibrium at the same temperature, $T_i = T$, then g_{*S} is simply equal to g_*. In our universe, this is the case until $t \approx 1\,\mathrm{s}$. Since s is proportional to the number density of relativistic particles, it is sometimes useful to write $s \approx 1.8\, g_{*S}(T)\, n_\gamma$, where n_γ is the number density of photons. In general, $g_{*S}(T)$ depends on temperature, so that s and n_γ cannot be used interchangeably. However, after electron-positron annihilation (see below), we have $g_{*S} = 3.94$ and hence $s \approx 7 n_\gamma$.

Since $s \propto a^{-3}$, the number of particles in a comoving volume is proportional to the number density n_i divided by the entropy density

$$N_i \equiv \frac{n_i}{s} \,.$$

If particles are neither produced nor destroyed, then $n_i \propto a^{-3}$ and N_i is a constant. An important example, of a conserved species is the total baryon number after baryogenesis, $n_B/s \equiv (n_b - n_{\bar{b}})/s$. A related quantity is the baryon-to-photon ratio

$$\eta \equiv \frac{n_B}{n_\gamma} = 1.8 g_{*S} \frac{n_B}{s} \,.$$

After electron-positron annihilation, $\eta \approx 7\, n_B/s$ becomes a conserved quantity and is therefore a useful measure of the baryon content of the universe.

Another important consequence of entropy conservation is that

$$g_{*S}(T)\, T^3\, a^3 = \text{const} \qquad \text{or} \qquad T \propto g_{*S}^{-1/3} a^{-1} \,.$$

Away from particle mass thresholds, g_{*S} is approximately constant and the temperature has the expected scaling, $T \propto a^{-1}$. The factor of $g_{*S}^{-1/3}$ accounts for the fact that whenever a particle species becomes non-relativistic and disappears, its entropy is transferred to the other relativistic species still present in the thermal plasma, causing T to decrease slightly more slowly than a^{-1}. We will see an example of this phenomenon in the next section.

Expansion history

As we have seen in Chapter 2, the Friedmann equation relates the Hubble expansion rate to the energy density of the universe. At early times, the universe is dominated by relativistic species and curvature is negligible. Hence, the Friedmann equation reads

$$H^2 = \left(\frac{1}{a}\frac{da}{dt}\right)^2 = \frac{\rho}{3M_{\rm Pl}^2} \simeq \frac{\pi^2}{90}\, g_* \,\frac{T^4}{M_{\rm Pl}^2}\,.$$

This is a single equation relating the expansion history of the universe to its temperature. We need one more equation to close the system for $a(t)$ and $T(t)$. Previously, we used the approximate equation of state for radiation, $w \approx 1/3$, which through the continuity equation determines $\rho(a)$. More precisely, we can substitute $T \propto g_{*S}^{-1/3} a^{-1}$ into (3.55). Away from mass threshold, this reproduces the result for a radiation-dominated universe, $a \propto t^{1/2}$, but we see that there is a slight change in this scaling every time $g_{*S}(T)$ changes.

When $a \propto t^{1/2}$, we have $H = 1/(2t)$ and the Friedmann equation leads to

$$\frac{T}{1\,\mathrm{MeV}} \simeq 1.5\, g_*^{-1/4} \left(\frac{1\,\mathrm{sec}}{t}\right)^{1/2} .$$

It is a useful rule of thumb that the temperature of the universe 1 second after the Big Bang was about $1\,\mathrm{MeV}$ (or $10^4\,\mathrm{K}$), and evolved as $t^{-1/2}$ before that. As we will show next, one second after the Big Bang was, in fact, an interesting moment in the history of the universe.