4 Thermodynamics in an expanding universe

4.1 Phase space density

As we look out in space we can see the history of the universe unfolding in front of our telescopes. However, at redshift $z = 1090$ our line of sight hits the last scattering surface, from which the cosmic microwave background (CMB) radiation originates. This corresponds to $t = 380000$ years. Before that the universe was not transparent, so we cannot see further back in time. However, the isotropy of the CMB indicates that matter was distributed almost homogeneously and isotropically in the early universe, and the spectrum of the CMB shows that this matter, the “primordial soup” of particles, was in thermal equilibrium. Therefore we can use thermodynamics to calculate the history of the early universe. As we will see, this calculation leads to predictions testable by observation (big bang nucleosynthesis, in particular, has been successfully tested). We will now derive the thermodynamics of the primordial soup starting from statistical physics. Note that we only deal with the statistical physics of a gas of particles: thermodynamics of the gravitational degrees of freedom is poorly understood, and will not be relevant for our discussion. Also, the interactions responsible for thermal equilibrium are those of non-gravitational physics. The only role of gravity here is to determine the expansion of space.

From elementary quantum mechanics we are familiar with the “particle in a box”. Let us consider a cubic box, whose edge is $L$ (and volume $V = L^3$), with periodic boundary conditions. Solving the Schrödinger equation gives us the energy and momentum eigenstates, with possible momentum values

$$\vec{p} = \frac{\hbar}{L}(n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \quad (n_i = 0, \pm 1, \pm 2, \ldots).$$

(4.1)

The state density in momentum space (number of states / $\Delta p_x \Delta p_y \Delta p_z$) is thus

$$\frac{L^3}{\hbar^3} = \frac{V}{\hbar^3},$$

(4.2)

and the state density in phase space $\{(\vec{x}, \vec{p})\}$ is $1/\hbar^3$. If the particle has $g$ internal degrees of freedom (e.g. spin), we have

$$\text{density of states} = \frac{g}{\hbar^3} = \frac{g}{(2\pi)^3} \left(\hbar \equiv \frac{\hbar}{2\pi} \equiv 1\right).$$

(4.3)

This result is true even for relativistic momenta. The state density in phase space is independent of the volume $V$, so we can apply it to arbitrarily large systems (including an infinite universe).

For much of the early universe, we can ignore interaction energies between particles. Then the particle energy is

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

(4.4)

where $p \equiv |\vec{p}|$ is the magnitude of the three-momentum (not pressure!), and the states available for the particles are the free particle states discussed above.

Particles fall into two classes, fermions and bosons. Fermions obey the Pauli exclusion principle: no two fermions can be in the same state.
In thermodynamic equilibrium the *distribution function*, or the expectation value $f$ of the occupation number of a state, depends only on the energy of the state. According to statistical physics, it is

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

where $+$ is for fermions and $-$ is for bosons. (In the case of fermions, for which $f \leq 1$, $f$ gives the probability that a state is occupied.) This equilibrium distribution has two parameters, the *temperature* $T$, and the *chemical potential* $\mu$. The temperature is related to the energy density in the system and the chemical potential is related to the number density $n$ of particles in the system. Note that since we use the relativistic formula for the particle energy $E$, which includes the mass $m$, the mass is also “included” in the chemical potential $\mu$. Thus, in the nonrelativistic limit both $E$ and $\mu$ differ from the corresponding quantities of nonrelativistic statistical physics by $m$, in such a way that $E - \mu$ and the distribution functions remain the same.

If there is no conserved particle number in the system (this is true for e.g. a photon gas), then $\mu = 0$ in equilibrium.

The particle density in phase space is the density of states times their occupation number,

$$\frac{g}{(2\pi)^3} f(\vec{p}).$$

We get the particle density in (ordinary) space by integrating over the momentum space. We thus have the following quantities:

\[
\begin{align*}
\text{number density} & \quad n_i = \frac{g_i}{(2\pi)^3} \int f_i(\vec{p}) d^3 p \\
\text{energy density} & \quad \rho_i = \frac{g_i}{(2\pi)^3} \int E_i(\vec{p}) f_i(\vec{p}) d^3 p \\
\text{pressure} & \quad p_i = \frac{g_i}{(2\pi)^3} \int \frac{|\vec{p}|^2}{3E_i} f_i(\vec{p}) d^3 p.
\end{align*}
\]

The index $i$ here labels different particle species, which have different masses $m_i$ and corresponding energies $E_i(\vec{p}) = \sqrt{p^2 + m_i^2}$. The above discussion applies separately to each particle species.

We won’t need it, but let’s note for the sake of completeness that the general expression for the energy-momentum tensor for a single species is

$$T^\alpha_\beta(t, \vec{x}) = \frac{g}{(2\pi)^3} \int \frac{d^3 p}{E} p^\alpha p_\beta f(t, \vec{x}, \vec{p}),$$

where the four-momentum is $p^\alpha = (E, \vec{p})$, with $p^\alpha p_\alpha = -m^2$.

### 4.2 Equilibrium distributions

If particle species $i$ has the above distribution for some $\mu_i$ and $T_i$, we say the species is in *kinetic equilibrium*. If the system is in *thermal equilibrium*, all species have the same temperature, $T_i = T$. If the system is in *chemical equilibrium* (“chemistry” here refers to reactions where particles change into other species), the chemical
potentials of different particle species are related according to the reaction formulae. For example, if we have a reaction

$$i + j \leftrightarrow k + l,$$  

(4.11)

then

$$\mu_i + \mu_j = \mu_k + \mu_l.$$  

(4.12)

Thus all chemical potentials can be expressed in terms of the chemical potentials of conserved quantities, e.g. the baryon number chemical potential, \(\mu_B\). There are thus as many independent chemical potentials as there are independent conserved particle numbers. For example, if the chemical potential of particle species \(i\) is \(\mu_i\), then the chemical potential of the corresponding antiparticle is \(-\mu_i\).

As the universe expands, \(T\) and \(\mu\) change in such a way that the energy continuity equation is satisfied and conserved quantum numbers remain constant. In principle, an expanding universe is not in equilibrium. The expansion is however so slow that the particle soup usually has time to settle close to local equilibrium. (And since the universe is homogeneous, the local values of thermodynamic quantities are also global values). From the remaining numbers of fermions (electrons and nucleons) in the present universe, we can conclude that in the early universe we had \(|\mu| \ll T\) for them when \(T \gg m\). (We don’t know the chemical potentials of the three neutrino species, but they are usually assumed to be small, too.) If the temperature is much greater than the mass, \(T \gg m\), the ultrarelativistic limit, we can approximate \(E = \sqrt{p^2 + m^2} \approx p\).

For \(|\mu| \ll T\) and \(m \ll T\), we approximate \(\mu = 0\) and \(m = 0\) to get the following formulae

\[
\begin{align*}
n &= \frac{g}{(2\pi)^3} \int_0^\infty \frac{4\pi p^2 dp}{ep/T \pm 1} = \begin{cases} 
\frac{3}{4\pi^2} \zeta(3) g T^3 & \text{fermions} \\
\frac{1}{\pi^2} \zeta(3) g T^3 & \text{bosons}
\end{cases} \\
\rho &= \frac{g}{(2\pi)^3} \int_0^\infty \frac{4\pi p^3 dp}{ep/T \pm 1} = \begin{cases} 
\frac{7}{8} \frac{\pi^2}{30} g T^4 & \text{fermions} \\
\frac{\pi^2}{30} g T^4 & \text{bosons}
\end{cases} \\
p &= \frac{g}{(2\pi)^3} \int_0^\infty \frac{4\pi p^3 dp}{ep/T \pm 1} = \frac{1}{3} \rho = \begin{cases} 
1.0505 n T & \text{fermions} \\
0.9004 n T & \text{bosons}
\end{cases}
\end{align*}
\]

(4.13)

(4.14)

(4.15)

For the average particle energy we get

\[
\langle E \rangle = \frac{\rho}{n} = \begin{cases} 
\frac{7\pi^4}{180\zeta(3)} T \approx 3.151 T & \text{fermions} \\
\frac{\pi^4}{30\zeta(3)} T \approx 2.701 T & \text{bosons}
\end{cases}
\]

(4.16)

In the above, \(\zeta\) is the Riemann zeta function, with \(\zeta(3) \equiv \sum_{n=1}^\infty n^{-3} = 1.20206\).

If the chemical potential vanishes, \(\mu = 0\), there are equal numbers of particles and antiparticles. If \(\mu \neq 0\), we find for fermions in the ultrarelativistic limit \(T \gg m\)
(i.e. for \( m = 0 \), but \( \mu \neq 0 \)) the "net particle number"
\[
 n - \bar{n} = \frac{g}{(2\pi)^3} \int_0^\infty dp \frac{4\pi p^2}{4\pi p^2} \left( \frac{1}{e^{(p-\mu)/T} + 1} - \frac{1}{e^{(p+\mu)/T} + 1} \right)
\]
\[
 = \frac{gT^3}{6\pi^2} \left( \frac{\pi^2 \mu}{T} + \left( \frac{\mu}{T} \right)^3 \right)
\]
and the total energy density
\[
 \rho + \bar{\rho} = \frac{g}{(2\pi)^3} \int_0^\infty dp \frac{4\pi p^3}{4\pi p^3} \left( \frac{1}{e^{(p-\mu)/T} + 1} + \frac{1}{e^{(p+\mu)/T} + 1} \right)
\]
\[
 = \frac{7g \pi^2 T^4}{8^3 15} \left( 1 + \frac{30}{7\pi^2} \left( \frac{\mu}{T} \right)^2 + \frac{15}{7\pi^4} \left( \frac{\mu}{T} \right)^4 \right).
\]

Note that the last forms in equations (4.17) and (4.18) are exact, not just truncated series. (The difference \( n - \bar{n} \) and the sum \( \rho + \bar{\rho} \) lead to a nice cancellation between the two integrals. We don’t get such an elementary form for the individual \( n, \bar{n}, \rho, \bar{\rho} \), or the sum \( n + \bar{n} \) and the difference \( \rho - \bar{\rho} \) when \( \mu \neq 0 \).)

In the nonrelativistic limit, \( T \ll m \) and \( T \ll m - \mu \), the typical kinetic energies are much below the mass \( m \), so we can approximate \( E = m + p^2/2m \). The second condition, \( T \ll m - \mu \), leads to occupation numbers \( \ll 1 \), a dilute system. This second condition is usually satisfied in cosmology when the first one is. (It is violated in systems of high density, such as white dwarf stars and neutron stars.) We can then approximate
\[
e^{(E-\mu)/T} \pm 1 \approx e^{(E-\mu)/T},
\]
so that the boson and fermion expressions become equal\(^1\), and we get (exercise)
\[
n = g \left( \frac{mT}{2\pi} \right)^{3/2} e^{-m-\mu}/T
\]
\[
\rho = n \left( m + \frac{3T}{2} \right)
\]
\[
p = nT \ll \rho
\]
\[
\langle E \rangle = m + \frac{3T}{2}
\]
\[
n - \bar{n} = 2g \left( \frac{mT}{2\pi} \right)^{3/2} e^{-m/T} \sinh \frac{\mu}{T}.
\]

In the general case, where neither \( T \ll m \), nor \( T \gg m \), the integrals don’t give elementary functions, but \( n(T), \rho(T), \text{etc.} \) need to be calculated numerically for the region \( T \sim m \).\(^2\)

By comparing the ultrarelativistic \( (T \gg m) \) and nonrelativistic \( (T \ll m) \) limits we see that the number density, energy density, and pressure of a particle species falls exponentially as the temperature falls below the mass of the particle. We have not so far made assumptions about the interactions that are responsible for

\(^{1}\)This approximation leads to what is called Maxwell–Boltzmann statistics; whereas the previous exact formulae give Fermi–Dirac (for fermions) and Bose–Einstein (for bosons) statistics.

\(^{2}\)If we use Maxwell–Boltzmann statistics, i.e., we drop the term \( \pm 1 \), the integrals give modified Bessel functions, e.g. \( K_2(m/T) \), and the error is often less than 10%. 

maintaining equilibrium. In the cosmological case, these include annihilation and particle-antiparticle pair formation. At high temperatures, these reactions balance each other, but as the temperature falls below the mass, the thermal particle energies are not sufficient for pair production any more, so the reactions happen only in the annihilation direction. The process of particle-antiparticle annihilation takes place mainly (about 80%) during the temperature interval $T = m \rightarrow \frac{1}{2} m$, as shown in figure 1. It is thus not an instantaneous event, but takes several Hubble times.

Figure 1: The fall of energy density of a particle species, with mass $m$, as a function of temperature (decreasing to the right).

### 4.3 Effective number of degrees of freedom

According to the Friedmann equation the expansion of the universe is governed by the total energy density

$$\rho(T) = \sum_i \rho_i(T),$$

where $i$ runs over particle species. Since the energy density of relativistic species is much greater than that of nonrelativistic species, it suffices to include the relativistic species only. (This is true in the early universe, but not at late times. Eventually the rest masses of the particles left over from annihilation begin to dominate and we enter the matter-dominated era.) We thus have

$$\rho(T) = \frac{\pi^2}{30} g_\ast(T) T^4, \quad (4.25)$$

where

$$g_\ast(T) = g_b(T) + \frac{7}{8} g_f(T),$$

and $g_b = \sum_i g_i$ over relativistic bosons and $g_f = \sum_i g_i$ over relativistic fermions. For pressure we have $p(T) \approx \frac{1}{3} \rho(T)$.

The above is a simplification of the true situation: Since the annihilation takes a long time, there are long periods when the annihilation of some particle species is going on, and its contribution disappears gradually. Using the exact formula for $\rho$ we define the effective number of degrees of freedom $g_\ast(T)$ as

$$g_\ast(T) \equiv \frac{30}{\pi^2} \frac{\rho}{T^4}. \quad (4.26)$$

We also define

$$g_{\ast p}(T) \equiv \frac{90}{\pi^2} \frac{p}{T^4} \approx g_\ast(T). \quad (4.27)$$
When there are no annihilations taking place, \( g_p = g_s = \text{const} \Rightarrow p = \frac{1}{3} \rho \). From the Friedmann equation it then follows that \( \rho \propto a^{-4} \), so we have and \( \rho \propto T^4 \) and \( T \propto a^{-1} \). We will soon calculate the scale factor-temperature relation more precisely (including the effects of annihilations).

### 4.4 Redshift of momenta

The momentum of freely moving particles redshifts with the expansion of the universe as

\[
p(t_2) = \frac{a(t_1)}{a(t_2)} p(t_1) .
\]  

Let us now show that it follows that ultrarelativistic non-interacting particles stay in kinetic equilibrium.

At time \( t_1 \) a phase space element \( d^3 p_1 dV_1 \) contains

\[
dN = \frac{g}{(2\pi)^3} f(\vec{p}_1) d^3 p_1 dV_1
\]

particles, where

\[
f(\vec{p}_1) = \frac{1}{e^{(p_1 - \mu_1)/T_1} + 1}
\]

is the distribution function at time \( t_1 \). At time \( t_2 \) these same \( dN \) particles are in a phase space element \( d^3 p_2 dV_2 \). How is the distribution function at \( t_2 \), given by

\[
\frac{g}{(2\pi)^3} f(\vec{p}_2) = \frac{dN}{d^3 p_2 dV_2},
\]

related to \( f(\vec{p}_1) \)? Since \( d^3 p_2 = (a_2/a_1)^3 d^3 p_1 \) and \( dV_2 = (a_2/a_1)^3 dV_1 \), we have

\[
dN = \frac{g}{(2\pi)^3} \frac{d^3 p_1 dV_1}{e^{(p_1 - \mu_1)/T_1} + 1} \quad (dN \text{ evaluated at } t_1)
\]

\[
= \frac{g}{(2\pi)^3} \frac{(a_2/a_1)^3 d^3 p_2 (a_2/a_1)^3 dV_2}{e^{(a_2/a_1)p_2 - \mu_1)/T_1} + 1} \quad (\text{rewritten in terms of } p_2, dp_2, \text{ and } dV_2)
\]

\[
= \frac{g}{(2\pi)^3} \frac{d^3 p_2 dV_2}{e^{(a_2/a_1)p_2 - \mu_2)/T_2} \quad (\text{defining } \mu_2 \text{ and } T_2),
\]

where \( \mu_2 \equiv (a_1/a_2)\mu_1 \) and \( T_2 \equiv (a_1/a_2)T_1 \). Thus distribution retains the thermal shape; the temperature and the chemical potential just redshift \( \propto a^{-1} \).

**Exercise.** Show that for a non-relativistic particle species, the distribution function retains the thermal shape as the universe expands, with \( T_2 = T_1 (a(t_1)/a(t_2))^2 \propto a(t_2)^{-2} \) and \( \mu(t_2) = m + (\mu(t_1) - m)T_2/T_1 \).

### 4.5 Scale factor-temperature relation

The relation between the temperature \( T \) and the scale factor \( a \) follows from the conservation of entropy. The entropy density is \( s = S/V \), is related to the effective number of entropy degrees of freedom \( g_{*s}(t) \) as

\[
s(T) \equiv \frac{2\pi^2}{45} g_{*s}(T) T^3 .
\]
Figure 2: The expansion of the universe increases the volume element $dV$ and decreases the momentum space element $d^3p$ so that the phase space element $d^3pdV$ stays constant.

The equation (4.31) defines $g_{ss}(T)$.

According to the second law of thermodynamics the total entropy of the universe never decreases: it either stays constant or grows. It turns out that entropy production in various processes in the universe is insignificant compared to the total entropy of the universe\(^3\), which is huge, and which is dominated by the relativistic species. Thus it is an excellent approximation to treat the expansion of the universe as adiabatic, so the entropy stays constant,

$$d(sa^3) = 0.$$  \hfill (4.32)

This gives the desired relation between $a$ and $T$:

$$g_{ss}(T)T^3a(t)^3 = \text{constant}. \hfill (4.33)$$

We will have much use for this formula.

In order to give substance to (4.33), we have to know what is $g_{ss}(T)$. For this we turn to the fundamental equation of thermodynamics,

$$E = TS - pV + \sum_i \mu_i N_i,$$

from which we get

$$s = \frac{\rho + p - \sum_i \mu_i n_i}{T}. \hfill (4.34)$$

In general, we get the entropy density by summing up the contributions to $\rho + p - \sum_i \mu_i n_i$ from all particle species, using the exact expressions given earlier. If

\(^3\)There may be exceptions to this in the very early universe, most notably the end of inflation, where essentially all of the entropy of the universe may have been produced. Recall that we are discussing only the entropy of matter: the entropy of gravitational degrees of freedom is a topic which remains poorly understood. Black holes are thought to have extremely large entropy.
$|\mu_i| \ll T$, we have for a single relativistic species

$$s = \frac{\rho + p}{T} = \begin{cases} \frac{7\pi^2}{180}gT^3 & \text{fermions} \\ \frac{2\pi^2}{45}gT^3 & \text{bosons} \end{cases}$$

Adding up all relativistic species and allowing for the possibility that some of them may have a kinetic temperature $T_i$ different from the temperature $T$ of those species that remain in thermal equilibrium, we get

$$g^*_s(T) = \sum_{\text{bos}} g_i \left( \frac{T_i}{T} \right)^4 + \frac{7}{8} \sum_{\text{fer}} g_i \left( \frac{T_i}{T} \right)^4$$

$$g_{ss}(T) = \sum_{\text{bos}} g_i \left( \frac{T_i}{T} \right)^3 + \frac{7}{8} \sum_{\text{fer}} g_i \left( \frac{T_i}{T} \right)^3 ,$$

and the sums are over all relativistic species of bosons and fermions.

If some species are “semirelativistic”, i.e. $m = O(T)$, then $\rho(T)$ and $s(T)$ have to be calculated from the integral formulae of section 4.2. Non-relativistic species give negligible contribution to the entropy.

As long as all species have the same temperature and $p \approx \frac{1}{3} \rho$, we have

$$g_{ss}(T) \approx g_s(T) .$$

We will see that this approximation breaks down in the real universe at around 1 s.