Conservation of entropy provides a powerful way of constraining the evolution of the temperature of particles in equilibrium. From the second law applied to a physical volume $V = a^3$, we have

$$T \, ds = d \left( p g \, V \right) + p g \, dV$$

where “$g$” here is to remind you that is for equilibrium particles (at temperature $T$, will skip subscripts) below.

$$\Rightarrow \left( \frac{\partial s}{\partial V} \right)_{V,T} = \frac{g + p}{T}$$

$$\Rightarrow \left( \frac{\partial s}{\partial t} \right)_{V} = \frac{V}{T} \, \frac{dp}{dt}$$

Now, the integrability condition that makes $s$ an exact differential is

$$\frac{\partial^2 s}{\partial t \partial V} = \frac{\partial s}{\partial V} \frac{\partial}{\partial t} \frac{\partial s}{\partial V}$$

which implies

$$\frac{2}{dt} \left[ \frac{g + p}{T} \right] = \frac{\partial}{\partial V} \left[ \frac{V}{T} \, \frac{dp}{dt} \right] \Rightarrow \frac{1}{T} \left( \frac{dp}{dt} + \frac{dp}{d\tau} \right) = \frac{g + p}{T^2} + \frac{1}{T} \, \frac{dp}{d\tau}$$

$$\Rightarrow \frac{dp}{dt} = \frac{g + p}{T}$$

Now, $T \, ds = d \left[ (g+p) \, V \right] - V \, dp \Rightarrow ds = \frac{d \left[ (g+p) \, V \right]}{T} - \frac{V \, dp}{T}$

$$= \frac{d \left[ (g+p) \, V \right]}{T} - V \, \frac{(g+p)}{T^2} \, dT = \frac{d \left[ \frac{(g+p) \, V}{T} \right]}{T}$$

$$\Rightarrow ds = \frac{d \left[ \frac{(g+p) \, V}{T} \right]}{T}$$

Now, recall that from stress-energy conservation $\sigma \left[ (\tau \nu) \right] = 0 \Rightarrow d(\sigma \nu) = -p \, dV$

$$\Rightarrow dS = 0 \quad \text{then entropy is conserved, therefore up to an arbitrary additive constant}$$

$$S = \frac{(g+p) \, V}{T}$$

Note that in practice there are some small departures from entropy conservation, i.e. $\nu \sigma \nu$, is not zero in short periods, but the $dS$ is very small compared to $d\phi \nu$, so negligible.
The entropy density is given by

\[ s = \frac{S}{V} = \frac{g + \rho}{T} \]

From this we see that the entropy is dominated by the relativistic particles, then to a very good approximation

\[ s = \frac{\alpha^2}{30} \frac{T^4}{V} \left(1 + \frac{1}{3}\right) g_*^S = \frac{2\alpha^2}{45} g_*^S T^3 \]

where we defined \( g_*^S = \sum_{\text{baryons}} g_i \left(\frac{T_i}{T}\right)^3 + \sum_{\text{fermions}} \frac{3}{8} g_i \left(\frac{T_i}{T}\right)^3 \)

Again, keeping in mind that not all relativistic particles may share the same \( T \) (some of them may have decoupled already, as we shall see later) - If \( T_i = T \)

then \( g_*^S = g_* \). Today \( g_*^S \neq g_* \); for \( t < 1 \) see \( g_*^S = g_* \).

From this we derive the important consequence,

\[ S \propto g_*^S T^3 a^3 = \text{const.} \]

as the universe expands

\[ \Rightarrow T \propto \left(g_*^S\right)^{-1/3} \frac{1}{a} \]

During periods where \( g_*^S = \text{const.} \) this recovers the approximate \( T \propto \frac{1}{a} \) that we used before. Note that when a particle becomes NR (as its mass becomes comparable to \( T \)), \( g_*^S \) drops, and therefore \( T \) drops slower than \( 1/a \). The reason is that the entropy of these particles gets picked up by the other particles in the bath (the same \( S \) is shared among smaller \( g_*^S \)), so effectively they don't cool as fast as \( 1/a \).

Entropy conservation tells us how particles that belong to the thermal bath cool off as the universe expands. However, how do the distributions...
of decoupled species evolve once they decoupled and thus fall out of thermal equilibrium?

Their evolution can be obtained from the fact that after decoupling a species evolves without interacting and therefore its distribution function \( f(p, t) = \frac{\text{d}n}{\text{d}p} \) is conserved. Then we know that \( n \propto a^{-3} \) and therefore \( p \propto a \) (this is completely analogous to the result for photons, where \( E \propto a \), and can be derived from the geodesic equation) - therefore, after decoupling we have

\[
f(p, t) = f_{\text{eq}} \left( \frac{p_{\text{eq}}}{a_{\text{dec}}} \right) \sim \frac{\text{d}n}{\text{d}p} \Rightarrow t \gg t_{\text{dec}}
\]

from how we can derive the evolution of temperature for decoupled species. We have two cases, as usual.

i) **Relativistic** while it decouples \( \lambda_{\text{mm}} \ll t_{\text{dec}} \)

\[
f(p, t) = f_{\text{eq}} \left( \frac{p_{\text{eq}}}{a_{\text{dec}}} \right) \sim \exp \left[ \frac{p a_{\text{dec}}}{T_{\text{dec}}} \right] \pm 1 \sim 1
\]

Notably, this is an equilibrium distribution, with an effective temperature

\[
T = T_{\text{dec}} \frac{a_{\text{dec}}}{a} \sim \frac{1}{a}
\]

Therefore, a species that decouples while relativistic evolves afterwards with a temperature \( T \sim 1/a \). From this we see that this species separately conserves its entropy, since \( S \sim T^3 a^{-1} \rightarrow S = 5a^3 = \text{const}. \)

From this distribution function we readily obtain,

\[
n = \left\{ \begin{array}{ll} \frac{\sqrt{3}}{314} & \text{for} \quad T \gg T_{\text{dec}} \left( \frac{a_{\text{dec}}}{a} \right)^3 \\
\end{array} \right.
\]

going as \( 1/a^3 \). This gives the number density after decoupling. Note that such species has a very similar number density.
to those in photons, so it will be around today (as e.g. the neutrino background).

As the universe expands, if \( m \) is not exactly zero, it will eventually reach a point where \( m \sim T \), so the decoupled particles become non-relativistic. However, the distribution function is still given by that of the relativistic case, as it must be conserved. The only difference is that now the energy \( E \sim m \) and therefore the number density and energy density are related by \( \gamma = m \frac{\beta}{c} \).

ii) Non-relativistic at decoupling, \( m \sim T \) (\( \mu \ll c m \))

Then we have:

\[
f (p, t) = \frac{f_{eq} (p, t)}{\alpha \frac{d \alpha}{d \epsilon} \epsilon^{1 + \epsilon}} \sim \exp \left[ - \frac{m + \frac{p^2}{2m} \alpha^2 \frac{d \alpha}{d \epsilon}}{T \epsilon} \right]
\]

\[
= \exp \left[ \frac{m + \frac{p^2}{2m} \frac{\alpha^2}{1 + \frac{1}{T \epsilon}}}{T} \right] \mu \ll c m
\]

We can reinterpret this **dissociation** from an equilibrium perspective

\[
\frac{m + \frac{p^2}{2m} \alpha^2}{T \epsilon} = \frac{m + \frac{p^2}{2m} - \mu}{T}
\]

From

\[
\frac{\alpha^2}{1 + \frac{1}{T \epsilon}} = \frac{p^2}{2m} \frac{1}{T} \Rightarrow T = T_{dec} \left( \frac{\alpha_{dec}}{\alpha} \right)^2 \sim \frac{1}{a_0^2}
\]

\[
\Rightarrow \frac{m}{T \epsilon} = \frac{m - \mu}{T} = \frac{m - \mu}{T \epsilon} \left( \frac{\alpha}{\alpha_{dec}} \right)^2 \Rightarrow \mu = m \left[ 1 - \left( \frac{\alpha_{dec}}{\alpha} \right)^2 \right]
\]

Therefore, after decoupling a NR species can be thought of having an equilibrium distribution with \( T \sim 1/a^2 \) and the above chemical potential.

Note that the number density that follows from this is

\[
n \sim g \left( \frac{mT}{2\pi} \right)^{3/2} \exp \left[ - \frac{(m - \mu)}{T} \right] \sim A \frac{a^3}{T} \sqrt{\text{constant from expression above for } \mu \frac{d \mu}{d \epsilon}}
\]
the arguments above tell us generically how species evolved after they decouple (in the limits $m \ll T$ and $m \gg T$, when $m \not= T$). Things are more complicated and cannot be mapped to equilibrium distributions. In order to know which case corresponds to a particular species we have to consider the mass spectrum and interactions in the standard model of elementary particles.

To describe what’s going on at temperature $T$ we need to understand physics at energies $E \sim T$. For $T < 0.1$ TeV (1 TeV), we have accelerators and understand the physics quite well. For $T > 1$ TeV, our predictions are based on extrapolations, particularly for $T > 10^{16}$ GeV things become very uncertain, e.g., naively at $10^{19}$ GeV (Planck scale) classical general relativity is not appropriate anymore and one must resort to quantum gravity (this may actually happen at much lower energies according to some modern ideas).

But for $T < 1$ GeV $< 10^{13}$ K things are very well understood, and this is where the standard hot big bang model operates.

Before we get into specific interactions, let us write the expansion rate in a useful way. For R&Q era we have:

\[
\left( \frac{a}{a_0} \right)^2 = 4H^2 = \frac{1}{4\pi^2} \rho_c = \frac{8\pi^2}{3} g_* \frac{\pi^2}{90} T^4
\]

\[
H = g_*^{1/2} T^2 \left( \frac{8\pi^2 G}{90} \right) = 1.66 \sqrt{G} g_*^{1/2} T^2 = 1.66 g_*^{1/2} \left( \frac{T}{1 \text{ MeV}} \right)^2
\]

Also:

\[
t = 0.3 g_*^{1/2} \left( \frac{\text{MeV}}{T} \right) \quad \Rightarrow \quad t \approx 2.4 g_*^{-1/2} \left( \frac{\text{MeV}}{T} \right)^2 \text{ sec}
\]

Remember $g_* \approx 10^{-5}$ for $T > 1$ MeV

\[
t \approx 1 \text{ sec} \quad @ \quad T = 1 \text{ MeV}
\]
Let's begin the discussion of the thermal history of the universe at \( T = 10^{12} \text{ K} \approx 35 \text{ MeV} \). At this temperature, the only relativistic degrees of freedom are: photons, neutrinos and electrons and positrons (recall more or less). We are at or below the \( W^\pm, Z^0 \) masses, and all quarks are already inside neutrons and protons (the quark-hadron phase transition happens at about \( 0.2 \text{ GeV} \)). We will assume all chemical potentials are zero. Then we have:

\[ \begin{align*}
\bar{\Theta}_T &= \frac{g_* S}{2} = g_{\text{baryons}} + \frac{7}{8} g_{\text{fermions}} = 2 + \frac{7}{8} \left[ 2 \times 2 + 3 \times 2 \right] = \frac{43}{8} \approx 10.75 \\
\Rightarrow \quad \frac{\Theta_T}{T^4} &= 1.66 \left( g_* ^{1/2} \right) \frac{T^3}{m_{\text{pe}}} = 5.4 \frac{T^2}{m_{\text{pe}}} 
\end{align*} \]

Neutrinos have no electric charge and they interact by weak interactions with electrons and positrons, and equilibrium is maintained by

\[ \nu \bar{\nu} \leftrightarrow e \bar{e}, \quad \nu e \leftrightarrow \bar{\nu} \bar{e} \]

The cross section is, as we discussed, roughly

\[ \sigma(E) \sim E^2 \left( \frac{g_*}{\mu^2 m_e^2} \right)^2 \sim E^2 \frac{2^4}{M_Z^4} \sim E^2 g_*^2 = G_F^2 T^2 \]

\[ \rho \sim E \sim M_Z \sim 90 \text{ GeV} \]

then, the interaction rate is

\[ T \sim \langle \nu \bar{\nu} \rangle \sim \frac{2(3) g_* T^3 g_F^2 T^2}{\pi^2} \sim 1.3 g_*^2 T^5 \]

\[ \Rightarrow \quad T \sim \frac{4}{3} T^3 \frac{m_{\text{pe}}}{G_F^2} \sim \left( \frac{T}{1.6 \times 10^{10} \text{ K}} \right)^3 \]

Therefore, \( \nu \)'s can be in \( Eq \) until \( T \sim 1.4 \text{ MeV} = 1.6 \times 10^{10} \text{ K} \) -- At this time \( T \approx T^* \), afterwards \( T \sim 1/a \), whereas for photons and electrons (while relativistic) also \( T \sim 1/a \). However, eventually when
T reaches 0.5 MeV, the $e^+e^-$ become NR and transfer their entropy to the photons, which makes them cool slightly slower. The neutrinos do not care since they've decoupled already and thus their entropy is separately conserved. Let's estimate what's going here. The idea is that as $T$ approaches 0.5 MeV we have

$$e^+e^- \rightarrow \gamma \gamma \quad \text{[with $\gamma$s getting thermalized by Compton scattering]}
$$

but the inverse process $\gamma \gamma \rightarrow e^+e^-$ becomes suppressed.

Therefore the number density $n_{e^+}n_{e^-}$ starts to drop exponentially (which is what means to be in EQ when a species becomes NR).

As the $e^+e^-$ become NR they cease to contribute to relativistic degrees of freedom, this leads to a change in $g^S_\ast$:

Before: \( \delta_1 e^+e^- \quad g^S_\ast = 2 + \frac{7}{6} \times 2 \times 2 = 11 \)

after: \( \delta \quad (g^S_\ast)' = 2 \)

Then we have

$$g^S_\ast T^3 = (g^S_\ast)' (T')^3$$

$$\Rightarrow \quad \frac{T'}{T} = \left( \frac{g^S_\ast}{g^S_\ast}' \right)^{1/3} = \left( \frac{11}{2} \right)^{1/3} \approx 1.4$$

Now, since up to this $T = T_0 = T_\gamma$, but after this the photons will have $T'$ whereas neutrinos continue with $T$ (both dropping as 1/u).

Therefore we have

$$\frac{T_\gamma}{T_0} \approx 1.4 \Rightarrow \quad \left[ \begin{array}{l} \text{today} \\ \text{after} \end{array} \right] \quad \frac{T_\gamma}{T_0} \approx \frac{2.70K}{1.4} \times 1.989K$$

$g^S_\ast$ does not change due to $e^+e^-$ annihilation.
After \( t = 3 \), the next interesting epoch is when energy density in radiation equals matter energy density. Now as radiation we just count \( v \) s and a generation of \( \sqrt{T} \), then

\[
P_R = \frac{\pi^2}{30} g_* T^4 = \frac{\pi^2}{30} \left[ 2 + 3 \times 2 \times \frac{7}{8} \times (\frac{4}{3})^{4/3} \right]^4 T^4
\]

\[= \frac{\pi^2}{30} \times 3.36 \times (\text{meV})^4 \times (1+\ell)^4 \]

\[\approx T_{1/2} \propto (1+\ell)^{4/3}\]

Whereas for matter we have \( p_m = \frac{3}{2} m^2 + 8 \times 10^{-47} \text{eV} \times (1+\ell)^3 \)

Table:

| \( 1+\ell_{eq} \) | \( = 3 \times 10^4 \times 2.32 \times 10^4 \) | \( \approx 3.45 \times 10^4 \) for present cosmological parameters
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<tr>
<td>or ( T_{eq} = T_0 (1+\ell_{eq}) = 5.5 \text{ eV} \times \Omega_m h^2 )</td>
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