E THERMODYNAMICS AND COSMOLOGY

The thermal history of the Universe combines three aspects: Firstly, the decrease of temperature of the cosmic photon bath with increasing scale factor, which is mediated by the recession motion of particles at which scattering processes take place or as a straightforward transformation effect, secondly, the decrease in the corresponding energy scale at which particle processes take place such as the formation of light nuclei in the early Universe and the formation of atoms, and lastly the equilibration of particle ensembles.

E.1 *Temperature evolution and FLRW-dynamics*

The subject of this chapter is the relationship between the temperature of cosmological fluids, in particular photons, and the geometry of the Universe, i.e. the scale factor a. In physics it is a common approach that a new phenomenon is traced back to the most fundamental measurements we can take, time intervals and distances. In this spirit the effect of fields on charges in electrodynamics is explained by considering the acceleration of a test charge and general relativity itself is a theory of how the measurements of time intervals and distances is affected by the presence of gravitational fields. Likewise, temperature as a phenomenon can traced back to mechanical measurements by means of a Carnot-engine. A Carnot-engine is a cyclic engine which operates between two heat reservoirs at different temperature and converts heat into mechanical energy at a fixed efficiency which only depends on the ratio between the two temperatures. It can be used as a thermometer to determine the temperature of one reservoir relative to the other by determining the heat flux and the amount of mechanical work. Mechanical work can be measured purely by measurements of time intervals and distances, for instance, the mechanical work can be used to accelerate a test object of a given mass. From this point of view it is perhaps not surprising that temperatures are affected by changes in the metric, as they influence the basic measurements of distances and time-intervals.

The Universe is filled with a photon background in which the photons outnumber baryons by a factor of about 10^9, implying that the photon temperature governs many of the particle reactions until they can decouple from the photons under certain conditions. The photons are in thermal equilibrium and their temperature decreases while the Universe expands, in face the relationship between photon temperature T and the scale factor a is $T \propto a$. It is very important to realise, however, that photons can neither equilibrate nor make transitions to a new equilibrium temperature without interacting with matter: This is a direct consequence of electrodynamics, which is linear and does not include direct scattering processes between photons. The change in temperature of the photons is caused in emission and absorption processes or mere scattering processes with charged particles taking place in an expanding space: Due to the relative motion between e.g. atoms in which photon emission and absorption processes one realises a decrease in photon wavelength with the Hubble expansion, and therefore a decrease in energy due to a general relativistic Doppler-effect. This mechanical picture can be viewed in a very abstract way: Due to the relative motion between emitting and absorbing atoms the photon gas undergoes a thermodynamic change of state and is relaxed, accompanied by a decrease in temperature $T \propto a$.

Equilibration takes place in interactions of photons with matter in which the photon number is not conserved. Photons (and in fact all relativistic ensembles with massless particles) have the curious property that many properties including their number in an ensemble at equilibrium is determined by the temperature (and the chemical potential). The number of photons changes if the system is brought to a different temperature by a non-adiabatic process which is at contrast with an ensemble of atoms, which can at fixed particle number assume any temperature. In fact, the number of photons can fluctuate as interactions take place where single photons are absorbed and more than one photon is emitted. This implies that a grand-canonical description needs to be used for photons, where the particle number is not fixed and photons may be generated or destroyed.

For this chapter, keep in mind that the density ρ under the Hubble-expansion with the scale factor a behaves according

$$\rho \sim a^{-3(1+w)} \tag{E.234}$$

with an equation of state parameter w. In particular one gets for radiation with $w = +1/3$ the scaling $\rho \propto a^{-4}$, which is commonly interpreted as a scaling of volume which dilutes the number density by a^{-3} together with an additional redshifting by another factor of a, as the photons are scaled to longer waverlength by increasing a.

At first, let's have a look at the 'textbook derivation' of the temperature evolution $T(a)$. From statistical mechanics we know that ideal, relativistic gases (photons) have an adiabatic index of $\kappa = 4/3$. Further, the Hubble-expansion is adiabatic (because there are no heat fluxes that would transport thermal energy away, as heat fluxes would violate the cosmological principle and because there is no decay of particles into photons which would effectively constitute a source of thermal energy) and therefore the thermal energy content is unchanged $\delta Q = 0$. Using the adiabatic invariant

$$T \underbrace{V^{\kappa-1}}_{V^{\frac{1}{3}}=(a^3)^{\frac{1}{3}}=a} = \text{const.} \tag{E.235}$$

we obtain the important result

$$Ta = \text{const.} \qquad \text{or} \qquad T \sim \frac{1}{a}. \tag{E.236}$$

As second approach, let's try a (hopefully) more intuitive way: We start with the thermal energy $E = k_B T$ and use the dispersion relation $E = cp$ for relativistic particles like photons (effectively, this is the point where this derivation becomes compatible with the previous one: The dispersion relation is equivalent to the relativistic adiabatic index). Now using the de Broglie-relation $p = \frac{h}{\lambda}$, we end up using $\lambda \sim a$ from the Hubble-expansion at

$$E = k_B T = cp = \frac{ch}{\lambda} \sim \frac{1}{a} \tag{E.237}$$

From both of the above derivations it can be concluded, that as the Universe increases by a, the temperature drops by $1/a$. The temperature T as a function of comoving distance (or equivalently, conformal lookback time), is shown in Fig. 6, for different cosmological models.

E.2 *Cosmic microwave background*

The Universe is filled with a thermal ensemble of photons, whose temperature drops as the Universe expands. Depending on the physical picture one adopts, there are

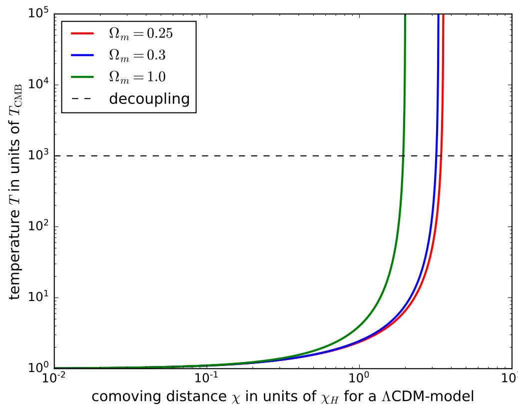

Figure 6: Temperature T *as a function of comoving distance* χ*, for 3 different* Λ*CDM cosmologies*

different views on the dependence of temperature with redshift: Clearly, the wavelength of each photon is redshifted with the Hubble-expansion and the photons are measured to have longer wavelengths at later times, and the ratio between observed wavelength to inital wavelength is proportional to $1/(1+z)$ or, equivalently, to the scale factor a. In order to link this change in wavelength to temperature, one can invoke three principes: Firstly, the momentum p of a photon in inversely proportional to wavelength λ, $p = h/\lambda$, with the Planck-constant h as the constant of proportionality, and secondly, the dispersion relation of photons is that of ultrarelativistic particles, $E = cp$. If one then assign the thermal energy $E = k_B T$ to an ensemble of photons in order to relate their typical energy to temperature, one obtains $k_B T = ch/\lambda$. As the wavelength λ is proportional to the scale factor, T must scale proportional to $1/a$. Using the photon dispersion relation $c = \lambda\nu$ which relates wavelength λ and frequency ν implies the inverse scaling of frequency, $\nu \propto a^{-1}$ and therefore $\nu \propto T$.

The same result can be obtained in a very different physical picture: Considering the photon fluid as a thermodynamic substance and the Hubble-expansion as a (reversible) change in volume by a factor a^3, one would derive the change in temperature with the adiabatic relation. Adiabatic changes in state are characterised by the absence of a heat flux, and clearly such a heat flux would violate the FLRW-symmetry assumptions. For an adiabatic change in state the quantity $TV^{\kappa-1}$ is constant, with the volume V, the temperature T and the adiabatic index κ of the substance. Photons as ultrarelativisitic particles have $\kappa = 4/3$, implying the relation $T \propto a^{-1}$ with $V \propto a^3$.

There is a nice consistency between both pictures: If the Universe was filled with thermal non-relativistic particles, their adiabatic index of $\kappa = 5/3$ would imply a dependence $T \propto a^{-2}$, which could likewise be derived by using a quadratic dispersion relation $E = p^2/(2m)$: Together with the definition of thermal energy $E = k_B T$ and the de Brogie-relation $p = h/\lambda$ this suggests $T \propto a^{-2}$ as well. One should be careful in generalising this result to other substances: The adiabatic index of $\kappa = 5/3$ applies to non-relativistic particles with 3 translational degrees of freedom. If the Universe was filled with a diatomic gas it would be wrong to derive a scaling $T \propto a^{-6/5}$ given its adiabatic index of $\kappa = 7/5$ on the basis of the three translational and two rotational degrees of freedom. Because only the translational degrees of freedom are affected (and the corresponding components of momentum redshifted), the gas would also cool down $\propto a^{-2}$.

It should be kept in mind that a photon gas always needs interactions with particles such as atoms to reach thermal equilibrium, because electrodynamics as a linear theory has perfect superposition and no scattering between the photons themselves (at least at the energies we are concerned with). Therefore, the increase in volume due to the Hubble expansion needs to be thought of as the increase in distance and the corresponding cosmological redshifting between emission and absorption of a photon at two locations: The photons are coupled to the Hubble expansion through scattering processes on advected particles.

The temperature of the photon background is sufficiently low at a scale factor of $a \simeq 10^{-3}$ to allow the formation of atoms from free nuclei and electrons. As the Universe becomes neutral scattering processes between photons and free electrons cease, the Universe becomes transparent to light and photons can propagate freely along straight lines: This corresponds to the release of the cosmic microwave background. Although, due to the FLRW-symmetries, the formation of atoms takes place at the same instant everywhere simultaneously, we perceive this process at a fixed distance isotropically around us: The spherical surface, from which the photons of the cosmic microwave background seem to emanate is called the surface of last scattering, or, the photosphere of the cosmic microwave background.

An estimate of the formation temperature of hydrogen atoms from the ionisation energy would correspond to about 10^4 Kelvin and not to the 3×10^3 Kelvin one finds in cosmology: In fact, the formation of atoms and therefore the release of the cosmic microwave background is delayed. The decoupling of the photons would be a very slow process, in which the rate of formation of atoms and their destrucion by photons with sufficient energy would slowly tilt towards the first process as the temperature decreases. Instead, there is a forbidden, two-photon transition from the $2s$-state to the ground state, which allows the generation of a photon population at a lower temperature along with a population of neutral atoms as they can not be reionised due to a deficit in photon energy.

The incredibly accurate data taken by the FIRAS-instrument onboard the COBE-satellite shows clearly that the CMB is described by a Planck-spectrum with proper Bose-Einstein statistics and not by an analogously constructed Wien-spectrum with Boltzmann-statistics, as illustrated by Fig. 7.

E.3 *Into and out of equilibrium*

Thermal equilibrium is maintained by collisions between particles, which implies a competition between two time-scales: The collision time scale t_c, at which particles exchange energy and momentum, and the Hubble-time scale, on which the temperature changes due to the expansion of the Universe: If $t_c \ll t_\mathrm{H}$, collisions between particles are frequent and thermal equilibrium can be maintained, but if $t_c \gg t_\mathrm{H}$, the system can drop out of thermal equilibrium. This happens necessarily at some point in the history of the Universe, because one can estimate t_H to be $t_\mathrm{H} = 1/\mathrm{H}(a) \propto a^2$ during radiation domination, whereas the collision rate $\Gamma = n\langle\sigma\upsilon\rangle$ with the number density n, the cross-section σ and the particle velocity υ implies a scaling of $t_c = \Gamma^{-1} \propto a^3$ due to the inverse proportionality to the particle number density. Therefore, $t_c/t_\mathrm{H} \propto a$ and thermal equilibrium can be maintained at early times, and can break down at late times.

Specifically, the time-evolution of the number density of particles follows a continuity equation,

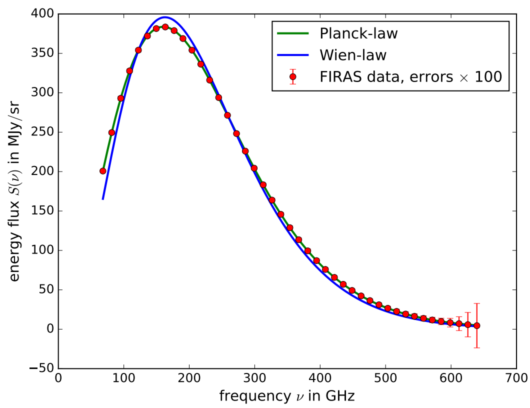

Figure 7: Spectrum of the cosmic microwave background as recorded by the FIRAS instrument onboard the COBE-satellite, with the best fitting Planck- and Wien-spectra in comparison

$$\dot{n} + \mathrm{div}(n\boldsymbol{\upsilon}) = 0 \tag{E.238}$$

which reduces to $\dot{n} + 3\mathrm{H}n = 0$ by substituting the Hubble-flow $\boldsymbol{\upsilon} = \mathrm{H}\boldsymbol{r}$, by assuming homogeneity of the particle density and by using that $\mathrm{div}\boldsymbol{r} = 3$. Then, the number density of particles has the solution $\mathrm{d}\ln n/\mathrm{d}t = -3\mathrm{H}$, which is solved by $n(t) \propto \exp(-3\mathrm{H}t)$ if H is constant, otherwise by $n(t) \propto \exp(-3\int \mathrm{d}t\mathrm{H})$. Relating this to the scale factor one can substitute the definition of the Hubble function, $\mathrm{H} = \dot{a}/a$, yielding $\mathrm{d}\ln n/\mathrm{d}t = -3\mathrm{d}\ln a/\mathrm{d}t$ with the solution $n \propto a^{-3}$, as expected: The substitution of the Hubble-law $\upsilon = \mathrm{H}r$ conserves homogeneity perfectly, and is in fact the only law that would allow this. As a proof, please remember that in an isotropic case one could substitute a generalised Hubble law $\upsilon \propto r^{\alpha}$ into the continuity equation, where the divergence is explicitly formulated in spherical coordinates,

$$\partial_i \upsilon^i = \frac{1}{r^2}\frac{\partial}{\partial r}(r^{2+\alpha}) = \frac{2+\alpha}{r^2}r^{1+\alpha} = \mathrm{H}(2+\alpha)r^{\alpha-1}, \tag{E.239}$$

which does not depend on r if $\alpha = 1$, implying that n can only change with time.

The time-evolution is modified if there are collisions present and if particles can be created in reactions,

$$\dot{n} + 3\mathrm{H}n = -\mathrm{Q} + \mathrm{S} = -\Gamma n\left(1 - \frac{n_{\mathrm{T}}^2}{n^2}\right) \tag{E.240}$$

with the collision rate $\mathrm{Q} = \langle\sigma\upsilon\rangle n^2$ and the particle creation rate S for which we make the ansatz $\mathrm{S} = \langle\sigma\upsilon\rangle n_{\mathrm{T}}^2$. Because both processes involve the collisions between particle pairs, the pair number density is relevant which is well approximated by the squared particle density. The particle density n should decrease if particles thermalise through collisions, which takes place at the rate Γ, and particles are created at the rate Γ from a thermal background, necessitating the proportionality to the density of thermal particles n_T. The number density of thermal particles n_T can be predicted from a dispersion relation and the suitable statistics.

Introducing the comoving number density $\mathrm{N} = na^3$ with the derivative $\dot{\mathrm{N}} = a^3(\dot{n} + 3\mathrm{H}n)$ yields

$$\dot{\mathrm{N}} = -\Gamma\mathrm{N}\left(1 - \frac{\mathrm{N}_\mathrm{T}^2}{\mathrm{N}^2}\right) \tag{E.241}$$

which can be rewritten by replacing the time variable t with the scale factor a,

$$\frac{\mathrm{d}\ln\mathrm{N}}{\mathrm{d}\ln a} = -\frac{\Gamma}{\mathrm{H}}\left(1 - \frac{\mathrm{N}_\mathrm{T}^2}{\mathrm{N}^2}\right) \tag{E.242}$$

by writing $\dot{\mathrm{N}} = a\mathrm{H}\mathrm{d}\mathrm{N}/\mathrm{d}a$. In this relation, the competition of time scales is clearly expressed by the prefactor Γ/H, which is large if $t_c \ll t_\mathrm{H}$ and collisions dominate, and conversely small if $t_c \ll t_\mathrm{H}$, in which case the Hubble expansion dominates. This prefactor changes the rate at which n can change if $\mathrm{N} \neq \mathrm{N}_\mathrm{T}$, and can effectively keep N constant even if $\mathrm{N} \neq \mathrm{N}_\mathrm{T}$ in the limit $\Gamma \ll \mathrm{H}$, for a dominating Hubble-expansion.

If a system is away from thermal equilibrium, the number N is larger than N_T, implying a positive bracket in the last equation, which causes N to decrease in time, meaning that the system is driven towards thermal equilibrium, which is reached at $\mathrm{N} = \mathrm{N}_\mathrm{T}$ where the evolution of N stops. If conversely, N_T is larger than N, the sign switches and N can increase and the system can freeze out, if the prefactor Γ/H allows it.

E.4 *Photon background as a thermodynamical ensemble*

The properties of a cosmological radiation background can be understood from the properties of a quantum system at thermal equilibrium. Distributing the particles in phase space needs to respect the Friedmann-symmetries, so one assumes homogeneity in configuration space and isotropy in momentum space for any cosmological observer, while one is free to choose the distribution in momentum space as a function of energy and the dispersion relation $\mathrm{E}(p)$ of the particles. Specifically, for photons one has as the ultrarelativitic dispersion relation $\mathrm{E}(p) = cp$ with the momentum $p = h/\lambda$, and the phase space density $n(p, \mathrm{T}) = 1/(\exp(cp/(k_\mathrm{B}\mathrm{T})) - 1)$ for bosons.

An ideal gas of photons has the interesting property that its chemical potential μ vanishes and the corresponding fugacity $\exp(\mu/(k_\mathrm{B}\mathrm{T}))$ is equal to one: This is related to the fact that the photon number is not constrained, due to emission and absorption processes, which cause the number of photons in the system to fluctuate. In equilibrium the Helmholtz free energy $\mathrm{F} = \mathrm{F}(\mathrm{T}, \mathrm{V}, \mathrm{N})$ is at a minimum, as it describes the energy of a system in thermal equilibrium at a given temperature T, volume V and particle number N. Because F follows by a Legendre transform from the internal energy U, $\mathrm{F} = \mathrm{U} - \mathrm{TS}$ replacing the entropy S by the temperature T one obtains for the differential $\mathrm{dF} = -\mathrm{SdT} - \mathrm{PdV} + \mu\mathrm{dN}$. The minimum condition implies that $\partial\mathrm{F}/\partial\mathrm{N} = \mu = 0$, meaning that the chemical potential for a system at constant temperature and volume vanishes, $\mu = 0$, in thermal equilibrium.

Radiation pressure and entropy of the thermal photon gas result from differentiation of the grand canonical potential $\mathrm{J}(\mathrm{T}, \mathrm{V}, n)$, which describes a system at equilibrium at fixed temperature, constant chemical potential and not performing mechanical work. Specifically, the grand canonical potential $\mathrm{J}(\mathrm{T}, \mathrm{V}, \mu)$ is defined as $\mathrm{J} = \mathrm{U} - \mathrm{TS} - \mu\mathrm{N}$ and by substituting the Euler-relation $\mathrm{U} = \mathrm{TS} - \mathrm{PV} + \mu\mathrm{N}$ it is readily shown to be $J = -PV$. The grand canonical potential has the differential $dJ = -SdT - PdV - Nd\mu$, which can be shown by substituting the Euler relation $dU = TdS - PdV + \mu dN$. It follows from the grand canonical partition sum Z by taking the logarithm,

$$J = -k_B T \ln Z. \tag{E.243}$$

The grand canonical partition sum Z is defined as

$$\ln Z = \frac{g}{(2\pi\hbar)^3} \int d^3x \int d^3p \ \ln\left(1 - \exp\left(-\frac{cp}{k_B T}\right)\right) \tag{E.244}$$

if the dispersion relation for ultrarelativistic particles $E(p) = cp$ is substituted for the energy and if their statistical weight is g, meaning that a single state can be occupied by g particles: Photons have spin 1, and being ultrarelativistic, there can only be two particles per state, $g = 2$. The expression for the grand canonical partition sum Z can be written in a closed form by integration by parts,

$$\ln Z = -\frac{gV}{(2\pi\hbar)^3} \int dp \, 4\pi p^2 \ln\left(1 - \exp\left(-\frac{cp}{k_B T}\right)\right) = \frac{gV}{(2\pi\hbar)^3} \int dp \, \frac{4\pi c}{3k_B T} p^3 \frac{1}{\exp\left(\frac{cp}{k_B T}\right) - 1} \tag{E.245}$$

while identifying the configuration space volume $V = \int d^3x$ and assuming isotropy in momentum space, and abbreviating $\beta = 1/(k_B T)$. The integration can be carried out by substituting $x = \beta cp$ and using the relation $\int dx \, x^n/(\exp(x) - 1) = \zeta(n+1)\Gamma(n+1)$,

$$\ln Z = \frac{gV}{(2\pi\hbar)^3} \frac{4\pi}{3} \left(\frac{k_B T}{c}\right)^3 \zeta(4)\Gamma(4). \tag{E.246}$$

The difference between the distribution functions for Bose-Einstein, Fermi-Dirac and Boltzmann statistics are shown in Fig. 8.

Already from the expression for Z it is apparent that the temperature must scale $\propto a^{-1}$. An adiabatic change of state implies that the system moves to a new temperature while the relative probabilites are unchanged: While the configuration space scales $\propto a^3$ and the momentum space $\propto a^{-3}$ due to the scaling of the photon momentum $p = h/\lambda \propto a^{-1}$, it is necessary for the temperature to scale $\propto a^{-1}$ in order for the partition sum to remain invariant. It is quite interesting to note that the rescaling of temperature is sufficient for particles obeying different dispersion relations, as long as this dispersion, i.e. the relation between energy and momentum is scale free. Any deviation from a power law would have the consequence that a rescaling affects high and low-energy particles differently, breaking the overall shape invariance under rescaling by a. In this way it is possible to derive simple scaling behaviours for ultrarelativistic particles with $E = cp$ or for classical particles with $E = p^2/(2m)$.

A very interesting illustration of the shape-invariance of the Planck-spectrum is Wien's displacement law: The shape of the spectrum itself defines a frequency scale, which needs to scale necessarily $\propto 1/a$ in order not to violate the dispersion relation. This is in fact realised in any definition of such a scale in the spectrum, for instance through the location of the maximum. $dS(\nu)/d\nu = 0$ yields a frequency

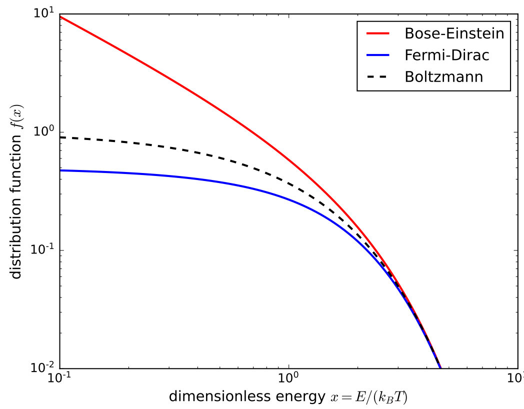

Figure 8: Bose-Einstein, Fermi-Dirac and Boltzmann-distribution functions

$\nu_{\max}$ = proportional to the temperature and hence proportional to $1/a$. Alternatively, one could consider the mean photon frequency $\bar{\nu} = \int \mathrm{d}\nu\, n(\nu)$, or the median frequency, which are all proportional to the temperature and hence inversely proportional to the scale factor a.

In the following we will derive the most important thermodynamical properties of a photon gas by an intuitive argument using a weighted integral over the occupation statistic and by a thorough derivation using the grand canonical partition sum: Starting with the internal energy one would use the phase space distribution $n(p, \mathrm{T})$ and the ultrarelativistic dispersion relation $\mathrm{E} = cp$ to collect the energy across the entire momentum space by carrying out the dp-integration, while the configuration space integration simply yields the volume of the system V:

$$\mathrm{U} = \frac{g\mathrm{V}}{(2\pi\hbar)^3} \int 4\pi p^2 \mathrm{d}p\ \mathrm{E}(p) \frac{1}{\exp\left(\frac{\mathrm{E}(p)}{k_\mathrm{B}\mathrm{T}}\right) - 1} \tag{E.247}$$

where again isotropy in momentum space was assumed, $\mathrm{d}^3p = 4\pi p^2 \mathrm{d}p$. The integral can be rewritten by integration by parts,

$$\int 4\pi p^2 \mathrm{d}p \ln\left(1 - \exp\left(\frac{cp}{k_\mathrm{B}\mathrm{T}}\right)\right) = \int 4\pi \frac{p^3}{3} \mathrm{d}p \frac{1}{\exp\left(\frac{cp}{k_\mathrm{B}\mathrm{T}}\right) - 1} \tag{E.248}$$

implying that $\ln \mathrm{Z} = \mathrm{U}/3$ and $p\mathrm{V} = \ln \mathrm{Z}$, i.e. the relation $p = \mathrm{U}/(3\mathrm{V})$ between pressure and internal energy as well as $\mathrm{J} = \mathrm{U}/3$. The total energy density of the radiation background is an expression of the Stefan-Boltzmann law. The total energy density can be evaluated to be equal to $\sigma_\mathrm{SB}\mathrm{T}^4$ with the Stefan-Boltzmann-constant σ_SB: This is in complete agreement with the fact that the number density $\int \mathrm{d}\nu\, n(\nu)$ is diluted $\propto a^{-3}$ and each photon's energy is redshifted by an additional factor of a^{-1}, resulting in a decrease of the energy density $\propto a^{-4}$, or equivalently, a proportionality of the energy density with T^4, as derived before.

The factor 1/3 in the relation between pressure and energy density follows from the same integral. The transfer of momentum onto a surface would be $2p\cos\theta$ under reflection and the flux of photons would be $c \cos\theta$. Therefore, assuming again isotropy of the photon momenta one would collect the total momentum transfer

$$P = \frac{g}{(2\pi\hbar)^3}\int d^3p\; 2cp\cos^2\theta\, n(p,T) = \frac{U}{3V} \tag{E.249}$$

by using spherical coordinates $d^3p = 2\pi p^2 dp \sin\theta d\theta d\phi$, where the azimuthal integration yields 2π and the polar one 1/3, for the range of angles $0 \le \theta \le \pi/2$.

For evaluating the integrals which were needed for computing thermodynamical quantities one can use the following trick and rewrite the phase-space distribution function $n(p,t)$ as a geometric series starting at $m = 1$. In general, one has

$$\sum_{m=0}^{\infty} q^m = \frac{1}{1-q} \quad\rightarrow\quad q\sum_{m=0}^{\infty} q^m = \sum_{m=1}^{\infty} q^m = \frac{q}{1-q} = \frac{1}{\frac{1}{q}-1}, \tag{E.250}$$

and therefore

$$\frac{1}{\exp(x)-1} = \sum_{m=1}^{\infty}\exp(-mx). \tag{E.251}$$

Substituting into the expressions obtained above yields

$$\int dx\, \frac{x^{n-1}}{\exp(x)-1} = \int dx\, x^{n-1}\sum_{m=1}^{\infty}\exp(-mx). \tag{E.252}$$

The integral can be solved by substitution $y = mx$, $dy = mdx$,

$$\int dx\, x^{n-1}\sum_{m=1}^{\infty}\exp(-mx) = \sum_{m=1}^{\infty} m^n \int dy\, y^{n-1}\exp(-y) = \zeta(n)\Gamma(n), \tag{E.253}$$

where one can identify Riemann's ζ-function and the Γ-function in the last step.

The entropy can be determined by differentiation of the grand canonical potential with respect to temperature, $dJ = -SdT - pdV + \mu dN$, and consequently

$$S = -\frac{\partial J}{\partial T} = \frac{\partial}{\partial T}(k_B T\ \ln Z) = k\left(\ln Z + \frac{1}{z}\frac{\partial Z}{\partial(k_B T)}\right) \tag{E.254}$$

or, equivalently by using $U = TS - pV = TS - J$ (if $\mu = 0$), such that $S = (U + J)/T = 4U/(3T)$. Therefore, the total entropy S is conserved because VT^3 = const from these considerations, in accordance with the entropy being constant for an adiabatic reversible change of state. The entropy density S/V scales $\propto T^3$ and therefore $\propto a^{-3}$.

The total number N of particles can be derived through an integral over the phase space density,

$$N = \frac{gV}{(2\pi\hbar)^3} \int 4\pi p^2 \mathrm{d}p \, \frac{1}{\exp\left(\frac{cp}{k_B T}\right) - 1} \tag{E.255}$$

or equivalently, by differentiation of the grand canonical potential with respect to μ,

$$N = -\frac{\partial J}{\partial \mu} = -k_B T \frac{\partial}{\partial \mu} \ln Z \tag{E.256}$$

For this purpose one needs to include a chemical potential in the definition of ln Z,

$$\ln Z = \frac{gV}{(2\pi\hbar)^3} \int 4\pi p^2 \mathrm{d}p \, \ln\left(1 - \exp\left(-\frac{cp + \mu}{k_B T}\right)\right) \tag{E.257}$$

which is set to zero after differentiating, yielding exactly the intuitive result. Evaluating the integrals shows the scaling of particle number density $N/V \propto a^{-3}$ due to the proportionality to T^3 and the conservation of the total number of particles N.

It suffices to replace the phase space density $n(p, T)$ by $n(p, T) = 1/(\exp(cp/(k_B T)) + 1)$ for the description of (massless) neutrinos: In complete analogy one obtains expressions for the particle number density $n = N/V$, the entropy density $s = S/V$ and the energy density $u = U/V$ with identical scaling behaviours with temperature, but with different numerical prefactors due to the changed sign in the phase space density.

There is a very interesting catch in the physical properties of the Universe's photon and neutrino backgrounds: Their temperature is not equal. Due to the annihilation of electron-positron pairs into photons there has been a source of thermal energy in the photon background, lifting it's temperature to 2.736 Kelvin, in comparison to the neutrino background which is at equilibrium at a temperature of 1.95 Kelvins. As there is essentially no coupling between photons and neutrinos, the two would never really equilibrate.

E.5 *Quantum-statistics and classical statistics*

The Universe is filled with particles at thermal equilibrium, whose thermodynamic properties can be derived using quantum statistics, i.e. Bose-Einstein-statistics for particles with integer spin such as photons and Fermi-Dirac-statistics for particles with half-integer spin, for instance neutrinos. The quantum mechanical description is necessary in particular at low energies, and this energy is characterised by the thermal wavelength λ_{th}. If the particle separation is smaller than the thermal wavelength, quantum mechanical interference becomes important and the behaviour deviates from that of a classical system: In contrast to classical statistics, quantum mechanical particles show constructive interference in the case of bosons, if two particles are interchanged, and destructive interference in the case of fermions. This impacts on the occupation statistics, because there can be arbitrarily many bosons in a single state due to constructive interference whereas there can only be a single fermion due to destructive interference. There is no such restriction for classical particles as they are distinguishable: In their time evolution it is always possible to track them through phase space, and a state with interchanged particles is clearly different.

The thermal wavelength corresponds to the de-Broglie wavelength $\lambda = ch/E$ of a photon with $k_B T$ of thermal energy, $\lambda_{th} = ch/(k_B T)$. It scales $\propto a$ with the scale factor,

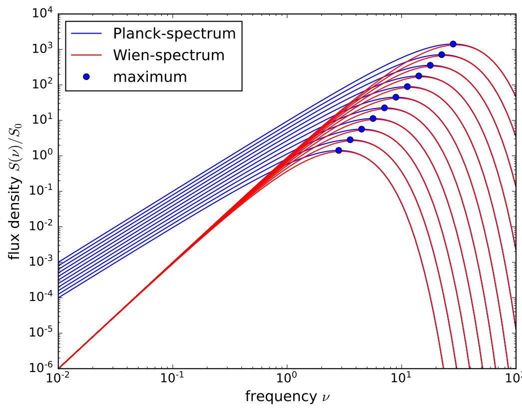

Figure 9: Planck- and Wien-spectra at different equilibrium temperatures

likewise the typical distance between particles of a given energy. Therefore, the photon gas is always characterised by the same Planck-distribution irrespective of scale factor, because for the same fraction of photons quantum mechanical interference is important, and the Hubble expansion will not affect the shape of the statistical distribution. The same argument holds for non-relativistic particles with a quadratic dispersion relation: $E = p^2/(2m)$, in which case the thermal wavelength would result in $\lambda_{\mathrm{th}} = h/\sqrt{2mk_{\mathrm{B}}T}$, which scales $\propto a$ in consistence with the scaling $T \propto a^{-2}$.

Planck- and Wien-spectra for different temperatures are compared to each other in Fig. 9, clearly showing an overabundance of photons at low energies in the correct quantum mechanical formulation relative to the classical prediction. In addition, the maxima show a clear linear trend to increase with increasing temperature as a manifestation of the Wien-displacement law.

E.6 *Radiation backgrounds*

Although the picture that the Universe is filled with photons, whose equilibrium temperature drops as the Universe expands is quite correct, it is worth pointing out two things: The change in wavelength or temperature is caused purely by the change in the metric, or if one adopts physical coordinates, by the a general relativistic Doppler-effect due to recession motion of the emitter. Because both the observer and the emitter in cosmology are following their world-lines in freely falling motion, one can be sure that locally for both the laws of special relativity are valid due to the equivalence principle. Because of the fact that in each frame all physical processes are determined by the laws of special relativity only, the redshifting effect on a photon can be unambiguously determined: In this respect, the interpretation would be that in the distant Universe atomic physics is exactly the same as it is here, and that we can measure a change in photon wavelength because we know the emission process under which a photon has been generated, for instance a certain atomic transition leading to a spectral line, and attribute the change in photon wavelength to the change in the metric between emission and absorption of a photon.

The Universe is filled with a homogeneous and isotropic radiation field in accordance with the symmetry assumption of the FLRW-metric. We perceive this photon background today as a blackbody radiation with an equilibrium temperature of $T_{CMB} = 2.725$ Kelvin. Looking along the backwards light cone towards earlier times, we perceive this temperature to be higher by a factor of $1/a$ (a is smaller than one in the past, implying a higher temperature) and there are physical processes, for instance emission and absorption processes with atoms, that take place at the corresponding temperature: The FLRW-symmetry assumptions make sure that at every time the photon background has the same temperature everywhere, but moving along the backward light cone of an observer one can see processes that are governed by temperature to set in at a certain redshift or, equivalently, distance relative to us.

For instance, atoms are formed in the Universe at a temperature of about 3000 Kelvin, and this formation of atoms takes place everywhere at the same age of the Universe, typically $10^1 2$ seconds after the Big Bang. For an observer today, this temperature is reached going back by about 1000 units in redshift, or to a scale factor of $a = 10^{-3}$, in order for the Universe to reach this temperature relative to the temperature of the background today. Again due to the FLRW-symmetries, the temperature is reached on the surface of a sphere with a distance of about $3\chi_H$ centered on us, on which we can observe radiation from the formation of atoms. The notion that we are surrounded by a photosphere of the cosmic microwave background does not imply that our position as observers is special: In fact any other observer at a different position would see an identical photosphere in perfect spherical symmetry around them with the same radius today.

The effect of different cosmological models or choices of cosmological parameters on the evolution of the background temperature is only relevant if a physical distance or time is assigned to a scale factor, because for this assignment the Hubble function is needed, which includes all density parameters and equations of state. The comoving distance along the backward light cone to the CMB photosphere can be computed as an integral

$$\chi_{CMB} = c \int_1^{a_{CMB}} \frac{\mathrm{d}a}{a^2 H(a)} \tag{E.258}$$

with $a_{CMB} = 10^{-3}$.

In some calculations is is practical to use the temperature as a time-variable, which is possible due to the monotonic relationship between scale factor and temperature: $T/T_{CMB} = 1/a$ implies $\mathrm{d}T/\mathrm{da} = -T_{CMB}/a^2$. For instance, one might estimate the thickness of the photosphere intuitively for a certain value of ΔT, inside which the temperature drops enough for atoms to form:

$$\Delta\chi \simeq \left|\frac{\mathrm{d}\chi}{\mathrm{d}t}\right| \Delta T = \left|\frac{\mathrm{d}\chi}{\mathrm{d}a}\frac{\mathrm{d}a}{T}\right| \Delta T = \frac{c}{H(a)}\frac{\Delta T}{T_{CMB}}. \tag{E.259}$$

If one very coarsely assumes in the next step that $\Delta T \simeq 0.1 T_{comb}$, one obtains $\Delta\chi \simeq 10^{-2.5}\chi_H$ with $T_{comb} = 3000$ Kelvin.

E.7 *Particle cosmology*

Extrapolating the dependence of temperature with the knowledge of the fact that the scale factor was much smaller in the past implies that the temperature in the early Universe was very high. There are two observations which support this idea, specifically, there is the cosmic microwave background on one side and the relative abundances of light chemical elements including their isotopes which are formed in the early Universe in a process called nucleosynthesis. Nucleosynthesis models constrain, in addition to nuclear reactions and the time passed between the initial and final temperatures, as well the relative abundances of neutrons and protons as its initial condition, with implications for baryongenesis at an even earlier stage.

E.7.1 Baryogenesis

In the course of the evolution of the early Universe, the temperature cools down sufficiently to allow the formation of baryons from quarks and gluons, i.e. there is a phase transition from the quark gluon-plasma to baryons such as protons and neutrons. At this point one can (and should) also ask the valid question, why there is more matter than antimatter in our Universe, for instance more protons than antiprotons, for which Sacharow has given three criteria:

1. The baryon number B has to be violated, e.g. by the asymmetric decay of a hypothetical X-particle precursing quarks and leptons,

$$X \to 2u \ 51\% \text{ vs. } \to \bar{d} + e^{+} \ 49\% \ \Delta B = 0.177 \tag{E.260}$$

   in comparison to the decay of the anti-particle $\bar{X}$,

$$\bar{X} \to 2\bar{u} \ 49\% \text{ vs. } \to d + e^{-} \ 51\% \ \Delta B = -0.157 \tag{E.261}$$

   ΔB is the baryon number weighted with the branching ratio.

2. CP- and P-symmetry have to be broken
3. The system has to be in thermal non-equilibrium

If all these criteria are fulfilled, baryons can outnumber anti-baryons. This is described e.g. as part of a grand unified theory of particle physics, it should be mentioned that all these theories are very uncertain.

E.7.2 Big bang nucleosynthesis

At a temperature scale of $\sim 10^{14}$ Kelvin the Universe experiences a phase transition at which protons and neutrons are formed from a plasma composed of quarks and gluons according to the rules of quantum chromodynamics, a quantum field theory that describes the interactions of these particles. Due to a slight mass difference between protons and neutrons (the neutron being more massive by about xxx Gev) one finds a slightly larger number of protons in the equilibrium of the β-process

$$n \leftrightarrow p + e^{-} + \bar{\nu}_e \tag{E.262}$$

After the formation of protons and neutrons the Universe continues to expand and to lower its temperature until temperatures are reached which allow the formation of light nuclei. Because neutrons are unstable with a lifetime of about 900 seconds, they partially decay until the formation of light nuclei starts at much lower temperatures. The neutron decay changes the abundance of protons significantly.

From the relation $T \sim \frac{1}{a}$ we can draw conclusions about the thermal history of our Universe as a was much smaller in history. For example at $a \sim 10^{-10}$ the corresponding temperature was $T \sim 10^{10}$K and therefore $\epsilon_{th} \sim MeV$, which allows nucleosynthesis in the early Universe shortly after the big bang. At $a \sim 10^{-3}$ the temperature was $T \sim 10^3$K or $\epsilon_{th} \sim e$V, which allows the formation of the first atoms. In the next chapters we will have a closer look at both mentioned periods.

For our initial conditions (at $\epsilon_{th} \sim$ GeV), the process

$$p + e^- \rightleftharpoons n + \nu_e \tag{E.263}$$

is allowed in both direction whereas after the freeze-out (T drops to $\epsilon_{th} \sim$ MeV) the process only happens from right to left (as known from 'normal' neutron decay with an $\bar{\nu}_e$). As the life-time of neutrons is ~ 15 min, the rate $\frac{n}{p}$ drops from $\frac{n}{p} = 1$ to $\frac{n}{p} \sim \frac{1}{7}$ before the fusion to deuterium D (at $T \sim 2$MeV)

$$p + n \rightleftharpoons \mathrm{D} + \gamma \tag{E.264}$$

sets in. The backwards process from right to left results from high energetic photons, which cause the dissociation of the deterium again, therefore fusion only sets in at $\epsilon_{th} \sim 100ke$V energies.

A crucial point for creating heavier element is the 'deuterium-bottleneck', as there has to be a decent amount of deuterium while still having left over neutrons. At this point the next question to ask is: How much time was there for production of deuterium in the right temperature-window? The answer is: Not much, from abundance measurements (hyperfine structure) we know of $\frac{n_\mathrm{D}}{n_p} \sim 3.5 \cdot 10^{-5}$, this limitation only leads to a creation of very light elements in the big-bang nucleosynthesis up to $A \sim 5...7$.

Back at the big bang nucleosynthesis, one could compare the photon background to the neutrino background from the produced ν_e's. For the derivation of the neutrino background one has to consider that neutrinos are fermions and therefore has to exchange the Bose- to a Fermi-Dirac-distribution and ends up at a pretty similar result (Remember that the Fermi-Dirac-distribution can be written as a difference of two Bose-distributions at different temperatures) which we don't discuss here. Just prior to nucleosynthesis, photons are produced by annihilation

$$e^+ + e^- \rightarrow 2\gamma \tag{E.265}$$

with temperature ($T \sim 10^{10.5}$K) is set by the electron rest-mass. With the knowledge that the entropy of fermions $S_{\text{fermion}} = \frac{7}{8} S_{\text{boson}}$, $S \sim T^3$ and the assumption that the entropy is conserved, one receives for the above process (E.265)

$$S_\gamma = S'_\gamma + S'_{e^+} + S'_{e^-} \tag{E.266}$$

and with the entropy relations put in

$$\left(2\frac{7}{8} + 1\right) T'^3 = T^3 \tag{E.267}$$

one ends up at $T = 1.4T'$ which implies that $T_\gamma = 2$K for the today's neutrino background. We further can now have a look at the baryon to photon ration

$$n_b = \frac{\rho_b}{m_p} = \frac{1}{m_p} \Omega_b \underbrace{\frac{3H_0^2}{8\pi G}}_{=\rho_{\text{crit}}} \tag{E.268}$$

Ω_b can be measured by X-ray observation of galaxy clusters and making use of the virial theorem. One obtains from these measurements $n_b \approx 1.1 \cdot 10^{-5} \Omega_b h^2 \mathrm{cm}^{-3}$ and $\Omega_b \approx 0.04$ or 10 atoms per cubic meter in the Universe today. Therefore the baryon to photon ratio is

$$\eta = \frac{n_b}{n_\gamma} \approx 2.7 \cdot 10^{-8} \Omega_b h^2 \approx 10^{-9} \tag{E.269}$$

n_γ in above's equation is received from the CMB-temperature and the usage of thermal equilibrium. With this result of approximate 10^9 more photons than atoms one can also imagine the first light elements being destroyed again by photodissociation.