

ASTR 425/525 Cosmology

Thermodynamics for Cosmologists

(Dated: September 29, 2025)

I. PARTICLE DISTRIBUTION FUNCTION AND NUMBER DENSITY

In cosmology, we are often interested in the collective behavior of a large number of particles, especially how they contribute to macroscopic quantities such as the energy density, the pressure, the entropy, etc. These particles are described by their positions $\{\mathbf{x}_i\}$ and their momenta $\{\mathbf{p}_i\}$ at some time t , where i runs over all the particles in the Universe. Since knowing all momenta and positions for all particles in the Universe is impossible, we instead introduce the *particle distribution function* $f(\mathbf{x}, \mathbf{p}, t)$ (also called phase-space density or occupation number), which determine the occupancy of the different position and momentum eigenstates in a given volume of phase space $d^3x d^3p$ centered around position $\mathbf{x}$ and momentum $\mathbf{p}$ at time t .

Now, how many possible eigenstates are there in a small phase-space volume $d^3x d^3p$? Quantum mechanics and the Heisenberg uncertainty principle tell us that no particle can be localized into a region of phase space smaller than $(2\pi\hbar)^3$. This means that the total number of eigenstates in a volume $d^3x d^3p$ is $d^3x d^3p / (2\pi\hbar)^3$. If the particle has g internal degrees of freedom (e.g. spin, color, etc.), then the *density of states* (or the number of states per unit phase-space volume) is thus

$$\frac{g}{(2\pi\hbar)^3}. \quad (1)$$

To compute the total number of particles present, we need to take this density of states, multiply it by the particle distribution function $f(\mathbf{x}, \mathbf{p}, t)$ (which determines which states are occupied and which ones aren't) and integrate over the whole phase space volume $d^3x d^3p$. In cosmology, we are not necessarily interested in the *total* number of particles, but rather in the number of particles per unit volume, which we refer to as the *number density*, n . So we generally do not perform the spatial integral over d^3x , and the number density is given by

$$n(\mathbf{x}, t) = g \int \frac{d^3p}{(2\pi)^3} f(\mathbf{x}, \mathbf{p}, t), \quad (2)$$

where we have used the standard natural units convention of setting $\hbar = 1$. Now, we are interested in applying these statistical mechanics arguments to cosmology, where the cosmological principle applies. On the one hand, homogeneity implies that the distribution function should be the same everywhere, so we have

$$f(\mathbf{x}, \mathbf{p}, t) = f(\mathbf{p}, t), \quad (3)$$

that is, it is independent of the position $\mathbf{x}$. Isotropy means that there is no special direction in the Universe, so the distribution function can only depend on the magnitude p of the momentum $\mathbf{p}$, that is,

$$f(\mathbf{p}, t) = f(p, t). \quad (4)$$

The number density then takes the form

$$n(t) = g \int \frac{d^3p}{(2\pi)^3} f(p, t). \quad (5)$$

Again, the number density is the number of particle of a given species per unit volume.

II. ENERGY DENSITY AND PRESSURE

The Friedmann and fluid equations that we have discussed previously are functions of the energy density and pressure from a given collection of particles. To obtain the energy density, we need to take the energy of each momentum eigenstate $E(p) = \sqrt{p^2 + m^2}$ and weigh it by the density of state $g/(2\pi)^3$ and the occupation number of each state $f(p, t)$ to obtain

$$\rho(t) = g \int \frac{d^3p}{(2\pi)^3} f(p, t) E(p). \quad (6)$$

In the above, we have assumed that the particles are essentially free, that is, that we can neglect the interaction energies between the particles. This is usually a very good approximation in cosmology. Meanwhile, the pressure P is given by

$$P(t) = g \int \frac{d^3p}{(2\pi)^3} f(p, t) \frac{p^2}{3E(p)}. \quad (7)$$

To understand where the factor of $p^2/3E$ comes from, see extra notes from Baumann (2022) posted on the website.

III. LOCAL THERMAL EQUILIBRIUM AND THE PARTICLE DISTRIBUTION FUNCTION

A set of particles is said to be in local thermal equilibrium (LTE) if the particles are both in *kinetic* and *chemical* equilibrium. To be in kinetic equilibrium, particles need to be able to exchange energy and momentum efficiently. If this is true, the particle distribution function takes either a *Fermi-Dirac* or *Bose-Einstein* form

$$f(p) = \frac{1}{e^{(E(p)-\mu)/T} \pm 1}, \quad (8)$$

where the $+$ sign is for fermions (half-integer spin) and the $-$ sign for bosons (integer spin). Here, μ is the *chemical potential* and T is the temperature. Again we have used natural units to set $k_B = 1$. In general, the chemical potential could be a function of the temperature. We emphasize here that in a universe with different particle species, each species i will in general have its own temperature T_i , chemical potential μ_i , energy density ρ_i , etc.

In the limit that $(E - \mu) \gg T$, the ± 1 in the denominator can be neglected and both distribution functions reduce to the *Maxwell-Boltzmann* distribution

$$f(p) = e^{-(E-\mu)/T}. \quad (9)$$

A particle species is said to be in *chemical* equilibrium with other species it interacts with if the sum of the chemical potentials on both sides of the reaction equation are the same. For example, if the reaction $1 + 2 \leftrightarrow 3 + 4$ is in chemical equilibrium then we have

$$\mu_1 + \mu_2 = \mu_3 + \mu_4. \quad (10)$$

Now, we are doing particle physics and cosmology here, not chemistry, and the type of reaction we are talking about here are particle scattering, particle decay, and particle annihilation. Consider for example double Compton scattering

$$e^- + \gamma \leftrightarrow e^- + \gamma + \gamma \quad (11)$$

which is in equilibrium at very high temperature in the early Universe. If this is the case, then we have

$$\mu_e + \mu_\gamma = \mu_e + 2\mu_\gamma, \quad (12)$$

from which we conclude that $\mu_\gamma = 0$. This is generally true in our Universe: the photon chemical potential is always nearly zero.

But to answer more generally what is the physical meaning of the chemical potential in cosmology, consider this. If a species has a nonzero chemical potential, it means that the number of particles and antiparticles of that species is *not* the same. That is, there is an asymmetry between number density of the particles and their corresponding anti-particles. The nice thing though is that if such asymmetry is present, the chemical potential of a particle species X and its anti-particle $\bar{X}$ in chemical equilibrium are simply related by

$$\mu_X = -\mu_{\bar{X}} \quad (13)$$

To see this, consider the annihilation channel $X + \bar{X} \leftrightarrow \gamma + \gamma$ together with the fact that $\mu_\gamma = 0$.