Thermodynamics of the Early Universe

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Abstract

In this paper, we explore the thermal history of the universe. We discuss the laws of thermodynamics and then the expansion of universe using Hubble's law and scale factor. We look at the radiation dominated universe and the entropy per comoving volume when the universe is in thermodynamic equilibrium. Using the concepts established, we then go on to find the neutron-proton ratio at the beginning and after the Deuterium bottleneck as well as calculate the time when the neutrinos decoupled from the primordial soup, which is approximately 1.31 seconds.

1 Introduction

Thermodynamics is the branch of physics that deals with temperature, work, heat and relates them to energy, entropy, and the physical properties of matter and radiation. It gives the qualitative and quantitative description about the system we are dealing with using the measurable macroscopic physical quantities, without diving into the microscopic constituents as in Statistical Mechanics. The physical description of universe is possible if is it filled with matter and radiation [1]. While at present, research is done for unknown components like dark matter and energy, we need not deal with them when describing the early universe [2]. Using the concepts in thermodynamics, we'll look into the expansion of the universe, radiation dominated universe and entropy, neutron-proton ratio at the beginning of Deuterium bottleneck and after it, and neutrino decoupling.

1.1 The First and Second Law of Thermodynamics

The fundamental relation in thermodynamics is given by the first law, which is essentially the formulation of the conservation of energy adapted for thermodynamic processes. For a system in equilibrium, the law can be written as,

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{1}$$

The equation implies the change in energy is the work done changing volume plus the temperature times change in entropy plus the chemical potential times the change in number of particles. If we assume the system is in equilibrium with negligible chemical potential or no change in particle number, we can write the equation as,

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \tag{2}$$

The Second law of thermodynamics establishes the concept of entropy as the physical property of the system. Clausius's statement of second law is, "No process is possible whose

[1]No observational evidence to disprove this [5]

[2]In the early universe, non-baryonic matter did not contribute to the formation of the elements.

sole effect is to transfer heat from a colder body to hotter body." Kelvin's formulation of this law is, "No process is possible whose sole effect is to extract heat from a single reservoir and convert it to work." Both these statements imply that the entropy of the universe can never decrease, which is the gist of the second law.

1.2 What is entropy?

Entropy is a measurable physical quantity which describes the state of disorder, randomness, or uncertainty. It is a state function, thus can be used to describe a system in its equilibrium state. At the state of thermodynamic equilibrium, the entropy is the highest. The thermodynamic formulation of entropy is,

$$\mathrm{d}S = \frac{\text{đ}Q}{T} \tag{3}$$

From statistical mechanics viewpoint, if Ω is the number of microstates of the system, the entropy is,

$$S = k_B \log \Omega \tag{4}$$

2 Geometry of the Universe and Hubble's Law

We'll now discuss the geometry of the universe and formulate concepts which we shall use later in the paper. At scales larger than a few mega-parsec, the universe seems highly symmetrical. The **Cosmological Principle** states that the universe is spatially isotropic (looks the same in every direction) and homogeneous (has constant density everywhere). In layman's terms, these mean that we do not occupy any special place in the large scale universe and an observer at any other place in the universe also observes the same properties of the universe. If we have a one dimensional universe with the Milky way as the reference origin, we can write the distance between one galaxy to another as,

$$ds = a(t)dx$$

Here, $a(t)$ is the scale factor, which scales the distance between our galaxy and the closest galaxy to us. Now, we can take the flat space R^3 as a 3-dimensional isotropic and homogeneous space. We can write the line element of the geometry in space and time of the universe as,

$$ds^2 = -c^2dt^2 + a^2(t)(dx^2 + dy^2 + dz^2) \tag{5}$$

Now, if we look at all event in time t, $dt = 0$. Then, the geometry of the universe is,

$$\mathrm{d}s^2 = a^2(t)(dx^2 + dy^2 + dz^2) \tag{6}$$

This can also be written as,

$$ds = a(t)dr, \quad dr = \sqrt{dx^2 + dy^2 + dz^2}$$

As time goes on, the coordinate grids in the 3-dimensional surface do not change, which implies the position of the galaxies do not change - rather, the distance between them changes because of the scale factor $a(t)$. This is essentially by virtue of an isotropic universe. Now, as the coordinates are expanding, the velocity of galaxy can be expressed as,

$$v = \frac{\mathrm{d}}{\mathrm{d}t}(ds) = dr\frac{\mathrm{d}a(t)}{\mathrm{d}t}$$

We multiply and divide both sides with $a(t)$ to get,

$$v = a(t)dr\frac{\mathrm{d}a(t)}{\mathrm{d}t}\frac{1}{a(t)} = ds\frac{\dot{a}(t)}{a(t)}$$

The Hubble's Law states that the galaxies are receding away from us with the velocity proportional to their distance from us - more distant galaxies recede faster than nearby galaxies. Mathematically, the relation is defined as,

$$v = H_0 ds$$

Here, H_0 is the Hubble's constant and the current value of the Hubble parameter. Comparing the above equation for the equation with velocity and scale factor, we can define the Hubble parameter as,

$$H(t) = \frac{\dot{a}(t)}{a(t)}$$

3 The Radiation Dominated Universe

The homogeneity and isotropy of the universe allows us to make one profound remark. As each coordinate box has the same temperature T, there is no heat flow. Hence, the universe can be assumed to behave adiabatically. Now, we will apply the first law of thermodynamics to the universe. If $\mathrm{d}U$ is the difference between the internal energy U of the given fixed coordinate volume at time $t + \delta t$ and U of the same coordinate volume at time t, and ρ is the energy density (energy per unit volume), then we can write,

$$\mathrm{d}U = \rho(t+\delta t)V_{\text{coord.}}a^3(t+\delta t) - \rho(t)V_{\text{coord.}}a^3(t) = V_{\text{coord.}}\frac{\mathrm{d}}{\mathrm{d}t}\left(\rho(t)a^3(t)\right)\mathrm{d}t \tag{7}$$

We also have $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$. Now, for adiabatic expansion, we can write the change in internal energy as,

$$\mathrm{d}U = -P(t)\frac{\mathrm{d}}{\mathrm{d}t}\left(V_{\text{coord.}}a^3(t)\right)\Delta t = -P(t)V_{\text{coord.}}\frac{\mathrm{d}}{\mathrm{d}t}\left(a^3(t)\right)\Delta t \tag{8}$$

So, comparing the two equations for $\mathrm{d}U$, equations 7 and 8, we can write,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\rho(t)a^2(t)\right) = -P(t)\frac{\mathrm{d}}{\mathrm{d}t}\left(a^3(t)\right)$$

In the radiation dominated universe, we can write the energy density as,

$$\rho(t) = \rho_r(t) + \rho_m(t) + \rho_d(t)$$

At t close to 0, ρ_r, the radiation energy density is dominant than the energy density of baryons and dark matter. Hence, we can write the relation between pressure and energy density for radiation as,

$$P(t) = \frac{1}{3}\rho_r(t)$$

Then, we can write,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\rho_r(t)a^2(t)\right) = -\frac{1}{3}\rho_r(t)\frac{\mathrm{d}}{\mathrm{d}t}\left(a^3(t)\right)$$

We take $\rho_r = ca^\alpha$ as the Ansatz (c and α are constants) and solve the above differential equation, we'll get $\alpha = -4$. Hence, we can write the energy density as,

$$\rho_r(t) = ca^{-4} \tag{9}$$

If t_0 is the present time, the ratio of energy density at time t is,

$$\frac{\rho_r(t)}{\rho_r(t_0)} = \frac{a^4(t_0)}{a^4(t)}$$

Hence, we get the relation,

$$\rho_r(t) = \rho_r(t_0)\left(\frac{a(t_0)}{a(t)}\right)^4 \tag{10}$$

The radiation made up of photons of wavelength λ are red-shifted (stretched) by the expansion, so increase proportionally to the scale factor $a(t)$. The corresponding frequency ω thus decreases by $1/a(t)$. As the energy of a photon is $\hbar\omega$, the energy gets smaller by $1/a(t)$. Hence, the $1/a^4(t)$ decrease of the radiative energy density comes when light is stretched. Using Stefan-Boltzmann law, we can also write the energy density as,

$$\rho_r = \sigma T^4 \tag{11}$$

Then, we can write the following relation,

$$T(t) = T(t_0)\frac{a(t_0)}{a(t)} \tag{12}$$

If $a(t_0) = a_0 = 1$ (scale factor at present is taken as 1), then we see that we start with an extremely hot plasma as $t \to 0$. So, just after Big Bang the universe is very hot. Moreover, if z is the redshift, then Lemaitre gave the relationship,

$$1 + z = \frac{1}{a(t)} \implies \frac{T(t)}{T(t_0)} = 1 + z \tag{13}$$

which we'll use in our calculations for neutrino decoupling time.

4 Entropy per comoving volume

We'll now go on to show that the entropy per comoving volume is conserved. The entropy is a function of volume V and temperature T, so we can write the differential as,

$$\mathrm{d}S = \frac{\partial S}{\partial V}\mathrm{d}V + \frac{\partial S}{\partial T}\mathrm{d}T \tag{14}$$

Now, as $U = \rho V$, where $V \propto a^3$ is the volume, and ρ is the energy density. We also let $V_{\text{coord.}} = 1$. Then, we can write using first law of thermodynamics,

$$\begin{aligned}
T\mathrm{d}S &= \mathrm{d}U + P\mathrm{d}V \\
&= \mathrm{d}(\rho V) + P\mathrm{d}V \\
&= \mathrm{d}(\rho V) + P\mathrm{d}V + V\mathrm{d}P - V\mathrm{d}P \\
&= \mathrm{d}(\rho V) + \mathrm{d}(PV) - V\mathrm{d}P \\
&= \mathrm{d}((\rho + P)V) - V\mathrm{d}P
\end{aligned}$$

Thus, we can write,

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}((\rho + P)V) - \frac{V}{T}\mathrm{d}P \tag{15}$$

Comparing this with the equation 14, we can write,

$$\frac{\partial S}{\partial V} = \frac{\rho + P}{T} \quad \text{and} \quad \frac{\partial S}{\partial T} = -\frac{V}{T}\frac{\mathrm{d}P}{\mathrm{d}T}$$

Now, for the above equations, we can write the derivatives,

$$\begin{aligned}
\frac{\partial^2 S}{\partial T \partial V} &= -\frac{\rho + P}{T^2} \\
\frac{\partial^2 S}{\partial V \partial T} &= -\frac{1}{T}\frac{\mathrm{d}P}{\mathrm{d}T}
\end{aligned}$$

We have the equality of mixed partial derivatives (Schwarz's theorem), so,

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \implies \mathrm{d}P = \frac{\rho + P}{T}\mathrm{d}T$$

Using the above, we can write equation 15 as,

$$\begin{aligned}
\mathrm{d}S &= \frac{1}{T}\,\mathrm{d}((\rho + P)V) - \frac{V}{T}\left(\frac{\rho + P}{T}\right)\mathrm{d}T \\
&= \frac{1}{T}\,\mathrm{d}((\rho + P)V) - \frac{V}{T^2}(\rho + P)\mathrm{d}T \\
&= \mathrm{d}\left[\frac{(\rho + P)V}{T} + \text{constant}\right]
\end{aligned}$$

The above relation implies that upto some additive constant, the entropy is,

$$S = \frac{(\rho + P)V}{T}$$

The equation for energy conservation says $\mathrm{d}((\rho + P)V) = V\mathrm{d}P$, which implies $\mathrm{d}S = 0$. This condition means,

$$S = \frac{(\rho + P)V}{T} = \text{constant}$$

Hence, we see that the entropy per comoving volume is conserved.

5 The Proton-Neutron Ratio

The age of the universe in seconds is given by the formula [5]

$$t_s = \frac{2.42}{\sqrt{g}T_{\mathrm{MeV}}^2}$$

Here, g is the spin degeneracy factor. The temperature is measured in MeV. This equation also approximates that the temperature of the universe around one second is 1 MeV. At these temperatures, protons and neutrons are in a dynamic equilibrium - they get converted into each other mediated by the weak force.

$$p + e^- \leftrightarrow n + \mu_e$$
$$n + e^+ \leftrightarrow p + \bar{\mu}_e$$

As neutrons are more massive than protons, we find their abundance less as the conversion of a neutron to a proton is less likely than a conversion of a proton to neutron. We can approximate the chemical potential of these particles as an ideal gas. The chemical potential of an ideal gas can be written as,

$$\mu = k_B T \ln\left(\frac{n\lambda_T^3}{g}\right)$$

Here, n is the density of the particles, which is given by N/V, where N is the number of particles and V is the total volume, λ_T is the thermal De Broglie wavelength, g is the spin degeneracy factor. If μ_P is the chemical potential of proton and μ_N is the chemical potential of neutron, during thermal equilibrium, their chemical potentials are equal. So, we can write,

$$\mu_P = \mu_N \tag{16}$$

As both proton and neutron are spin half particle, we will have, $g = 2s + 1 = 2(1/2) + 1 = 2$ for both of them. We can write the energy as,

$$k_B T \ln\left(\frac{n_P\lambda_P^3}{2}\right) + m_P c^2 = k_B T \ln\left(\frac{n_N\lambda_N^3}{2}\right) + m_N c^2 \tag{17}$$

The rest mass energy is added to the chemical potential of both the particles as if we introduce one more proton to the primordial plasma, it changes the energy by mc^2. Now, at a defined time t, the temperature is well defined and constant. Hence, using equation 17, we can write the ratio of density of neutron to proton as,

$$\frac{n_N}{n_P} = \left(\frac{m_N}{m_P}\right)^{3/2} \exp\left(-\frac{(m_N - m_P)c^2}{k_B T}\right) \tag{18}$$

We introduce some simplifications to the above equation as $Q = (m_N - m_P)c^2 \approx 1.29$ MeV and $(m_N/m_P)^{3/2} = 1.002$. Thus, at equilibrium, the neutron to proton ratio can be approximated as,

$$\frac{n_N}{n_P} = \exp\left(-\frac{Q}{k_B T}\right)$$

For $Q = 1.29$ MeV, we get corresponding value of $k_B T \approx 1.5 \times 10^{10}$ K, where we expect $n_N = n_P$. At $T \ll 1.5 \times 10^{10}$ K, we expect $n_N \ll n_P$. Now, to observe neutrons in the present universe, the neutron-proton equilibrium must break down in the early universe. As the temperature of the universe drops, the conversion reaction becomes slow compared to the age of the universe. At the time of the universe $t \approx 3$ seconds, $k_B T = 0.8$ MeV, $T = 9 \times 10^9$ K, the interaction rate is dropping quickly as the density and the temperature of the universe decline - thus there are no subsequent conversions. This is when the neutron freeze-out occurs, and the neutron-proton ratio is,

$$\left(\frac{n_N}{n_P}\right)_{\text{freeze out}} = \exp\left(-\frac{1.29}{0.8}\right) \approx 0.199 \approx \frac{1}{5}$$

6 The Deuterium Bottleneck

After the neutron freeze-out, the reaction that appreciably changes the number of neutrons is the neutron decay,

$$n \to p + e^{-} + \mu_e$$

The half-life of neutrons is around 887 seconds. If there were no reactions to preserve neutron within stable nuclei, the observable universe today would be pure hydrogen. So, the reaction that preserves the neutrons is deuteron formation.

$$p + n \leftrightarrow d + \gamma$$

Deuteron is the nucleus of the hydrogen isotope, deuterium. At $t \approx$ few seconds, the temperature of the universe is not much lower than the energy in the above exothermic reaction, 2.225 MeV. So, around this time, as there are million more photons than baryons, there are sufficient photons with energy greater than 2.225 MeV to destroy the newly formed Deuterium. Thus, the universe must expand further so that the radiation temperature decreases sufficiently enough for the formation rate of D to exceed the photo-dissociation rate. This happens at around $T = 8 \times 10^{8}$ K, and time $t \approx 300$ seconds. At this point, the neutron-proton ratio falls by the factor,

$$f = \exp\left(-\frac{300}{887}\right) = 0.71$$

Hence, the neutron-proton ratio falls to ,

$$\frac{n_N}{n_P} = 0.71 \times \frac{1}{5} \approx \frac{1}{7}$$

Hence, the temperature is low enough for the neutrons and protons to combine through chain of nuclear reactions to form deuterium, and then helium. Deuterium essentially creates a bottleneck in the production of heavier atoms, hence this is called ”Deuterium Bottleneck” and the proton-neutron ratio is 1/7 at this time.

7 Neutrino Decoupling

We have already seen that once the rate of weak interactions is slower than the characteristic rate of expansion of the universe, the dynamic equilibrium between neutron-proton is not maintained and the abundance of neutrons to protons freezes in at a value 1/5. At this time, when the temperature of the universe was around 1 MeV $= 1.16 \times 10^{10}$ K, the neutrinos decoupled from the primordial soup as they go across the universe without scattering at all. We now use the relation for the cosmological redshift in equation 13. Then, we can compare the temperature of the radiation emitted at the time of neutrino decoupling to the current temperature of the Cosmic Microwave Background (CMB) as,

$$1 + z = \frac{T}{T_0}$$

As we have $T_0 = 2.73$ K, the redshift from the decoupling time is,

$$1 + z = \frac{T}{T_0} = \frac{1.16 \times 10^{10}}{2.73} = 4.25 \times 10^{9} \implies a = \frac{1}{1+z} = \frac{1}{1 + (4.25 \times 10^{9})} = 2.35 \times 10^{-10}$$

For the radiation dominated universe, we can write the Friedmann equation as [7],

$$H^2 = \frac{8\pi G}{3}\rho_r \tag{19}$$

Now, using the equation 10 and the current scale factor $a(t_0) = 1$, we can write the Hubble parameter as,

$$H = \sqrt{\frac{8\pi G}{3}\frac{\rho_r(t_0)}{a^4(t)}}$$

Let ρ_c is the critical matter density required to explain the expansion of the universe without dark energy or radiation. Then, if ρ_{r0} and ρ_{c0} represent the current radiation energy density and critical matter density, we can write the current radiation density parameter as,

$$\Omega_{r0} = \frac{\rho_{r0}}{\rho_{c0}}$$

Then, as $H_0^2 = (8\pi G/3)\rho_{c0}$, the Hubble parameter is,

$$H = \frac{1}{a^2}\sqrt{\frac{8\pi G}{3}\Omega_{r0}\rho_{c0}} = \frac{H_0}{a^2}\sqrt{\Omega_{r0}}$$

At present $H_0 = 2.19 \times 10^{-18}\text{s}^{-1}$. So, the present value of critical density is,

$$\rho_{c0} = \frac{3H_0^2}{8\pi G} = \frac{3 \times (2.19 \times 10^{-18})^2}{8\pi \times 6.67 \times 10^{-11}} = 8.58 \times 10^{-27}\ \text{kg/m}^3$$

Then, the time when neutrinos decoupled after the Big Bang is,

$$t = \frac{1}{2H} = \frac{a^2}{2H_0\sqrt{\Omega_{r0}}} \tag{20}$$

The density parameter comes from both photons and neutrinos, which contribute about 68% of the density parameter by photons. Hence, using the relation with the energy density, the total radiation density parameter is,

$$\Omega_{r0} = \frac{E_{r0}}{c^2\rho_{c0}} + 0.68\frac{E_{r0}}{c^2\rho_{c0}} = 1.68\frac{\pi^2(k_BT)^4}{15\hbar^3c^5\rho_{c0}}$$

We have $\hbar = 1.05 \times 10^{-34}$ Js, $c = 3.00 \times 10^8$ m/s, $\rho_{c0} = 8.58 \times 10^{-27}$ kg/m^3. Hence, using these values, we get,

$$\Omega_{r0} = 1.68\frac{\pi^2(1.38 \times 10^{-23} \times 2.73)^4}{15(1.05 \times 10^{-34})^3(3.00 \times 10^8)^5 \times 8.58 \times 10^{-27}} = 9.23 \times 10^{-5}$$

Then, using the equation 20, we can calculate the time as,

$$t = \frac{(2.35 \times 10^{-10})^2}{2 \times 2.19 \times 10^{-18} \times \sqrt{9.21 \times 10^{-5}}} \approx 1.31\ \text{seconds}$$

Hence, the neutrinos decoupled from the primordial soup of the universe around 1.31 seconds after the Big Bang.

8 Conclusion

We see that the universe is expanding with time, and the second law of thermodynamics implies that the universe started from a low entropy state and with increase in time the entropy of the universe is increasing. Assuming an isotropic and homogeneous universe, the expansion of the universe can be modeled as an adiabatic process, which also gives the relation that the temperature is directly proportional to the cosmological redshift. For the universe in thermodynamic equilibrium, the entropy per comoving volume is shown to be conserved. The neutron-proton ratio when neutrino freezeout occured is $1/5$ and at the time of Deuterium bottleneck is $1/7$. Using various relations, we then deduce that neutrinos decoupled from the primordial soup around 1.31 seconds after the Big Bang.

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