On the Sackur-Tetrode equation in an expanding universe

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In this work we investigate the thermodynamic properties satisfied by an expanding universe filled with a monoatomic ideal gas. We show that the equations for the energy density, entropy density and chemical potential remain the same of an ideal gas confined to a constant volume V. In particular the Sackur-Tetrode equation for the entropy of the ideal gas is also valid in the case of an expanding universe, provided that the constant value that represents the current entropy of the universe is appropriately chosen.

Keywords: Expanding universe; ideal gas; Sackur-Tetrode equation.

En el presente trabajo investigamos las propriedades termodinámicas que son satisfechas por un universo en expansión, el cual es lleno por un gas ideal monoatómico. Se prueba que las ecuaciones para la densidad de la energía, la densidad de la entropía y el potencial químico son las mismas que las de un gas ideal, el cual se encuentra confinado en un volumen V. En particular, la ecuación de Sackur-Tetrode, para la entropía del gas ideal continua siendo válido en el caso de un universo en expansión, siempre que el valor constante que representa la entropía del universo actual sea escojido adecuadamente.

Descriptores: Universo en expansión; gas ideal; ecuación de Sackur-Tetrode.

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1. Introduction

The thermodynamic properties of an ideal gas have been known since the beginning of the nineteenth century through the works of Clapeyron, Boltzmann and other. Although it is only a theoretical model, since the particles are considered isolatedly and not interacting with each other, the ideal gas is a model that reproduces with great precision most of the gases at high temperature and low pressure. At normal conditions such as standard temperature and pressure, most real gases behave qualitatively like an ideal gas. Many gases such as air, nitrogen, oxygen, hydrogen, noble gases, and some heavier gases like carbon dioxide can be treated like ideal gases within reasonable tolerances [1]. The theoretical model of the ideal gas tends to fail to describe substances at lower temperatures or higher pressures, when intermolecular forces and molecular size become important. It also fails for most heavy gases, such as water vapor [1]. These must be modeled by more complex equations of state.

Recently the model of the ideal gas has been object of several studies, both in journals of education and research. Among the studies related to education we can quote the spectral and thermodynamical properties of systems with noncanonical commutation rules [2], the exact calculation of the number of degrees of freedom of a rigid body composed of n particles [3], the theoretical aspects concerning the thermodynamics of an ideal bosonic gas trapped by a harmonic potential [4] and the description of the ideal gas free expansion obtained with the aid of a computational modeling [5]. We can also cite numerous research topics, including cosmological applications [6], interaction with a nonrelativistic Kaluza-Klein gas [7], statistical properties of a two dimensional relativistic gas [8] and Einstein's equations for spherically symmetric static configurations of ideal gas [9]. All this shows that the ideal gas model is still being widely exploited and sometimes generalized to many different applications.

The relationship between the internal energy U of an ideal gas and the pressure P is given by the equation of state $PV = (2/3)U$. This relationship is very close to that of a very important real system, the electromagnetic radiation, which satisfies $PV = (1/3)U$.

Recently there has been a great interest in the study of thermodynamic systems satisfying an equation of state in the general form $PV = \omega U$, with ω a constant, positive or negative. The main motivation is that several kinds of complementary astronomical observations indicate that the Universe is expanding in an accelerated manner [10]. In the context of general relativity, an accelerating stage and the associated dimming of type Ia Supernovae are usually explained by assuming the existence of an exotic substance with negative pressure sometimes called dark energy, with $\omega < -(1/3)$. (See [11] for a good review and [12] for a recent discussion including chemical potential.)

There are many candidates to represent this extra non-luminous relativistic component. In the case of cold dark matter cosmologies, for instance, it can be phenomenologically described by an equation of state of the form $PV = \omega U$. The case $\omega = -1$ corresponds to a positive cosmological constant, or vacuum energy, while for $\omega < -1$ we have the so called phantom dark energy regime [13], or phantom fluids. Indeed, in the standard lines of the thermodynamic, we have showed in Ref. 14 that it does not make sense to speak of phantom fluids for systems with null chemical potential.

In this article we consider only the case $\omega = 2/3$, which corresponds to a universe filled with a monatomic ideal gas. We will show that the evolution laws for energy, entropy and chemical potential are reduced to those of an ideal gas confined to a constant volume V, even though the laws of evolution seem to be quite different in an expanding universe.

In Sec. 2 we review the thermodynamic properties of a monoatomic ideal gas. In Sec. 3 we present the thermodynamics of an expanding universe with an equation of state in the general form. In Sec. 4 we consider the particular case of a universe filled with a monoatomic ideal gas, and we show that the same properties of the second section can be obtained. We finish by presenting a simple estimate for the entropy and chemical potential of a neutrino gas filling the universe, showing that this estimate is in accordance with the limits set by primordial nucleosynthesis theory.

2. The monoatomic ideal gas

Considering the classical thermodynamics, it is well known that the entropy of a classical ideal gas can be given only within a constant. For a monoatomic classical ideal gas, an exact expression can be reached using quantum considerations. At the beginning of the last century, around 1912, Hugo Tetrode and Otto Sackur independently developed an equation for the entropy using a solution of the Boltzmann statistic. This equation is named Sackur-Tetrode equation, and is represented by [15]

$$S = \frac{5}{2}k_B N + k_B N \ln\left(\frac{V}{N}\right) + \frac{3}{2}k_B N \ln\left(\frac{mk_B T}{2\pi\hbar^2}\right), \quad (1)$$

where $k_B = 1.381 \times 10^{-23}$J/K is the Boltzmann constant, N is the particle number, V is the volume, T the temperature of the gas, m is the mass of the particle and $\hbar = 1.054 \times 10^{-34}$J.s is the Planck constant. The last term represents the quantum correction. In classical thermodynamics this constant remains undefined, and it can be determined only through the quantum statistical treatment. This expression can be reduced to a more compact form

$$S = Nk_B \ln\left[\exp(5/2)\frac{V}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right]. \quad (2)$$

The monoatomic ideal gas satisfies the ideal gas law $PV = Nk_B T$ and its internal energy is given by

$$U = \frac{3}{2}Nk_B T. \quad (3)$$

The pressure P is related to the energy U by the equation of state

$$PV = \frac{2}{3}U. \quad (4)$$

Finally, the chemical potential of the ideal monoatomic gas can be obtained by

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}, \quad (5)$$

where $G = U + PV - TS$ is the Gibbs free energy. By substituting the above expressions we obtain

$$\mu = -k_B T \ln\left[\frac{V}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right]. \quad (6)$$

An interesting aspect about this equation is the negative sign. Why is it negative? This question was very well explored by Cook and Dickerson [16]: "Actually, in the classical limit, the quantity in square brackets is large, much greater than 1, making μ a negative number. This is so whenever T is large, and the volume per particle, V/N, is large compared to the cube of the thermal de Broglie wavelength $\lambda = h/\sqrt{3mk_B T}$. In fact, μ must be negative, because in order to add a particle, while keeping the entropy and volume constant, the particle must carry negative energy, or rather, it must be added while the internal energy of the ideal gas is allowed to decrease, by cooling". In the last section we make a simple application to a gas of neutrinos and we see that in fact the chemical potential is negative in our simplified model.

Followings we will consider that the volume varies, so it is more convenient to express the above equations in terms of the energy density $\rho \equiv U/V$, the particle number density $n \equiv N/V$ and the entropy density $s \equiv S/V$,

$$P = \frac{2}{3}\rho, \quad (7)$$

$$\rho = \frac{3}{2}nk_B T, \quad (8)$$

$$s = nk_B \ln\left[\frac{\exp(5/2)}{n}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right], \quad (9)$$

$$\mu = -k_B T \ln\left[\frac{1}{n}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right]. \quad (10)$$

Our aim is to show that these equations remain valid even in an expanding universe where the thermodynamical parameters are not constant.

3. Thermodynamics of an expanding universe

Let us consider that the universe is described by the homogeneous and isotropic Friedmann-Robertson-Walker geometry [17,18] and is filled with a fluid described by the general equation of state

$$P = \omega\rho, \quad (11)$$

where ω is a constant parameter.

The equilibrium thermodynamic states of a relativistic simple fluid obeying the equation of state (11) can be completely characterized by the conservation laws of energy, the number of particles, and entropy. In terms of specific variables ρ, n and s, the conservation laws can be expressed as

$$\dot{\rho} + 3(1+\omega)\rho\frac{\dot{a}}{a} = 0,$$

$$\dot{n} + 3n\frac{\dot{a}}{a} = 0, \quad \dot{s} + 3s\frac{\dot{a}}{a} = 0, \quad (12)$$

where $a \equiv a(t)$ is the scale factor of the evolution, or roughly speaking, the universe radius, so that $V \propto a^3$ varies with the universe expansion. The above equations have general solutions of the form:

$$\rho = \rho_0 \left(\frac{a_0}{a}\right)^{3(1+\omega)},$$
$$n = n_0 \left(\frac{a_0}{a}\right)^3, \quad s = s_0 \left(\frac{a_0}{a}\right)^3, \tag{13}$$

where ρ_0, n_0, s_0 and a_0 are present day (positive) values of the corresponding quantities. On the other hand, the quantities P, ρ, n and s are related to the temperature T by the Gibbs law

$$nTd\left(\frac{s}{n}\right) = d\rho - \frac{\rho + p}{n}dn, \tag{14}$$

and from the Gibbs-Duhem relation there are only two independent thermodynamic variables, say n and T. Therefore, by assuming that $\rho = \rho(T,n)$ and $P = P(T,n)$, one may show that the following thermodynamic identity must be satisfied

$$T\left(\frac{\partial P}{\partial T}\right)_n = \rho + P - n\left(\frac{\partial \rho}{\partial n}\right)_T, \tag{15}$$

an expression that remains locally valid even for out of equilibrium states [19]. Now, inserting the above expression into the energy conservation law as given by (12) one may show that the temperature satisfies

$$\frac{\dot{T}}{T} = \left(\frac{\partial P}{\partial \rho}\right)_n \frac{\dot{n}}{n} = -3\omega\frac{\dot{a}}{a}, \tag{16}$$

and assuming $\omega \neq 0$ a straightforward integration yields

$$T = T_0 \left(\frac{a}{a_0}\right)^{-3\omega}, \tag{17}$$

so that the Eqs. (13) can be written in terms of the temperature as

$$\rho = \rho_0 \left(\frac{T}{T_0}\right)^{(1+\omega)/\omega},$$
$$s = s_0 \left(\frac{T}{T_0}\right)^{1/\omega}, \quad n = n_0 \left(\frac{T}{T_0}\right)^{1/\omega}. \tag{18}$$

These relations simply tell us that today, when the temperature of the universe is T_0, these quantities are equal to ρ_0, n_0 and s_0, which represent constants still undefined. Let us talk a little about these constants, particularly s_0. Just as the classical ideal gas entropy is defined up to an additive constant, here we find the same problem because we can not calculate the current value of the entropy of the universe, neither the number of particles n_0 and energy densities ρ_0. We need some model to infer the values of these constants. The observational data and recent theoretical models constrain very accurately the values of these constants. In the last section we

will analyze a simple model of a gas of neutrinos and show that our estimate is in agreement with one of these models.

Finally, let us see how the expression for the chemical potential is. Using the relation (5), the chemical potential is given by

$$\mu = -\left[\frac{s_0 T_0 - (1+\omega)\rho_0}{n_0}\right]\frac{T}{T_0}. \tag{19}$$

Note that the negative sign was purposely left in evidence.

4. Universe filled with a monoatomic ideal gas

In order to shown that the equations of a monoatomic ideal gas remain valid even in an expanding universe, let us take $\omega = 2/3$ in the above equations:

$$\rho = \rho_0 \left(\frac{T}{T_0}\right)^{5/2}, \quad n = n_0 \left(\frac{T}{T_0}\right)^{3/2},$$
$$s = s_0 \left(\frac{T}{T_0}\right)^{3/2}, \quad \mu = -\left[\frac{s_0 T_0}{n_0} - \frac{5}{3}\frac{\rho_0}{n_0}\right]\frac{T}{T_0}. \tag{20}$$

A very interesting feature of these equations is that all of them have a temperature dependence very different from those of Eqs. (8)-(10). We also see that as the universe is cooling down, all these quantities decrease with evolution.

Let us consider the equation for the energy density. It can be written as

$$\rho = \rho_0 \left(\frac{T}{T_0}\right)^{5/2} = \rho_0 \left(\frac{T}{T_0}\right)\left(\frac{T}{T_0}\right)^{3/2}$$
$$= \rho_0 \frac{n}{n_0}\left(\frac{T}{T_0}\right) = \frac{\rho_0}{n_0 T_0}nT. \tag{21}$$

But this expression has exactly the same form as Eq. (8) if we define

$$\frac{\rho_0}{n_0 T_0} \equiv \frac{3}{2}k_B, \tag{22}$$

so that

$$\rho = \frac{3}{2}nk_B T. \tag{23}$$

Thus we see that the energy density of the expanding universe behaves exactly like that of an ideal gas. Furthermore, the expression (22) is very interesting, relating the present day values of the constants n_0, ρ_0 and T_0 with the Boltzmann constant k_B.

Regarding the entropy expression, apparently the Sackur-Tetrode Eq. (9) has nothing to do with the corresponding one of Eq. (20). In the first, the temperature dependence is logarithm, while in the second, it is a power law. But note that s_0 is a constant that needs to be determined, corresponding to the actual entropy of the universe. Defining the s_0 constant as

$$s_0 = k_B n_0 \ln\left[\frac{\exp(5/2)}{n_0}\left(\frac{T_0 m k_B}{2\pi\hbar^2}\right)^{3/2}\right] \tag{24}$$

and substituting in the entropy expression we have, after some algebraic manipulations

$$
\begin{aligned}
s =& s_0 \left(\frac{T}{T_0}\right)^{3/2} = s_0 \frac{n}{n_0} \\
=& nk_B \ln\left[\frac{\exp(5/2)}{n_0}\left(\frac{T_0 m k_B}{2\pi\hbar^2}\right)^{3/2}\right] \\
=& nk_B \ln\left[\exp(5/2)\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\frac{1}{n_0}\left(\frac{T_0}{T}\right)^{3/2}\right] \\
=& nk_B \ln\left[\frac{\exp(5/2)}{n}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right],
\end{aligned}
\tag{25}
$$

which is exactly the Sackur-Tetrode equation.

Finally, we analyze the chemical potential. Using the relations (22) and (24) and substituting,

$$
\begin{aligned}
\mu =& -\left[\frac{s_0}{n_0} - \frac{5}{3}\frac{\rho_0}{n_0 T_0}\right]T = -k_B T\left[\left(\frac{s_0}{k_B n_0} - \frac{5}{2}\right)\right] \\
=& -k_B T\left[\ln\left[\frac{\exp(5/2)}{n_0}\left(\frac{T_0 m k_B}{2\pi\hbar^2}\right)^{3/2} - \ln[\exp(5/2)]\right]\right] \\
=& -k_B T \ln\left[\frac{1}{n_0}\left(\frac{mk_BT_0}{2\pi\hbar^2}\right)^{3/2}\right] \\
=& -k_B T \ln\left[\frac{1}{n}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right],
\end{aligned}
\tag{26}
$$

exactly the same as obtained in (10).

Thus we show that all the equations of an ideal gas are still valid even in the case of an expanding universe.

5. Concluding remarks

We studied the thermodynamic properties satisfied by an expanding universe filled with a monoatomic ideal gas. We showed that, although the relationships appear to be different, when we define the constants ρ_0 and s_0 in a convenient way, the same relations of an ideal gas confined in a region of constant volume V are obtained.

In order to verify the above equations, we make some simple estimates with this model assuming that neutrinos can be represented by the equation of state of an ideal gas, satisfying $P = 2/3\rho$. This is a very rough approximation, but we will see that the results are in agreement with more sophisticated models. Neutrino cosmology is a very current topic of research in astrophysics [17,18].

The estimate for the current density of neutrino is of order $n_{\nu 0}=115.05\times10^6$ particles/m^3, which corresponds to $n_0=8.84 \times 10^{-40}$ GeV^3 in natural units [20], and the neutrino energy density is

$$
\rho_0 = 2.95 \times 10^{-15} \text{ J/m}^3 = 1.41 \times 10^{-51} \text{ GeV}^4.
$$

One of the successful predictions of primordial nucleosynthesis provide strong indirect evidence that for each neutrino flavor the relation (see page 180 of [18])

$$
\frac{n}{s} < 1
\tag{27}
$$

is satisfied. The primordial nucleosynthesis also sets an upper limit to the individual neutrino chemical potentials of [18]

$$
\mu < 8.9 \times 10^{-3} \text{ eV}.
\tag{28}
$$

Using the model of an ideal gas, we can estimate the entropy density s_0 of a neutrino gas filling the whole universe and then verify if this relation is satisfied today, when the temperature T_0 is of the order of the temperature of the cosmic microwave background, $T_0 = 2.75$ K. Taking the neutrino mass as $m_\nu = 0.01$ eV$= 1.78 \times 10^{-38}$ kg (a reasonable value), and substituting it into the Eq. (24), we get $s_0 = 1.28\times10^{-14}$ J/Km$^3 = 9.29\times10^8$/m^3. Thus we see that the relation (27) is satisfied, since we obtain $n_0/s_0 = 0.12$ in natural units.

Another important result is the calculation for the chemical potential of the neutrino gas filling the universe. Making the substitutions in the Eq. (20), we get $\mu = -1.76 \times 10^{-22}$ J $= -1.10 \times 10^{-3}$ eV for the current value of the chemical potential. We see that the relation (28) is satisfied and the negative sign shows that it is in agreement with what was previously discussed in Sec. 1.

Remember that the ideal gas model is valid for high temperatures, but in this work we are making estimates using a very low value to T_0, which is the temperature of cosmic background radiation of 2.75 K, and even so we get a good agreement with the predictions of other models. This shows that the ideal gas model is a powerful tool to make estimates and even obtain good results for some situations that apparently require more sophisticated models.

Acknowledgements

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20. In natural units the following conversion factors are valid (see page 499 of [18] for more conversion factors): 1 GeV=1.7827×10^{-27}kg; 1 GeV$^{-1} = 1.9733 \times 10^{-16}$m; 1 GeV $= 1.1605 \times 10^{13}$K.