

Note on the chemical potential of decoupled matter in the Universe

Th. M. Nieuwenhuizen^{1,2} and C. Pombo³

¹*Institute for Theoretical Physics, University of Amsterdam,
Science Park 904, P.O. Box 94485, Amsterdam, the Netherlands*

²*Center for Cosmology and Particle Physics, New York University,
4 Washington Place, New York, NY 10003, USA*

³*1 Washington Square Village, New York, NY 10012, USA*

Textbooks on cosmology exhibit a thermodynamic inconsistency for free streaming, decoupled matter. It is connected here to the chemical potential, which deviates from its equilibrium value $\mu = \alpha k_B T$, where α is the usual parameter of the Fermi-Dirac or Bose-Einstein distribution function.

PACS numbers: 04.70.Bw, 04.20.Cv, 04.20.Jb

I. MOTIVATION

In the textbooks on cosmology and astrophysics, such as the ones of Dodelson [1], Weinberg [2] and of Giunti and Kim [3], chapters on thermodynamics state that the pressure p and energy density $u = \rho c^2$ (ρ is the mass density, c the vacuum speed of light in vacuum) satisfy at temperature T the relation

$$\frac{dp}{dT} = \frac{u+p}{T}. \quad (1)$$

Dodelson mentions that in principle there occurs also the chemical potential, adding that it is usually irrelevant in cosmology [4]. These authors all rush to point out that (1) is satisfied for photons and other relativistic particles, where $u \sim T^4$ and $p = \frac{1}{3}u$, but they do not mention that it is violated in other cases. Indeed, for nonrelativistic matter, such as baryons, cold dark matter and non-relativistic neutrinos, where $u = nmc^2$, $p \ll u$, with n the particle density, this relation is violated. We seek here to explain the cause of this paradox.

Our main point will be that because thermodynamics should be valid beyond equilibrium, an old truth that has allowed to formulate thermodynamics for the glassy state [5], Eq. (10) below must substitute Eq. (1). Hereto we recall the relevant laws of thermodynamics, apply them to equilibrium and, next, to the out of equilibrium situation in the expanding universe.

II. THERMODYNAMICS

The first law states that the change of energy of the system, $U = \rho c^2 V$, is the sum of the heat added to the system, the work done on the system and energy gained by adding particles to the system,

$$dU = dQ + dW + \mu dN. \quad (2)$$

where μ is the gain in energy per particle when one keeps $dQ = dW = 0$. With the second law $dQ = T dS$ and the

mechanical work for a change of the volume V , $dW = -pdV$ this yields

$$dS = \frac{dU + pdV - \mu dN}{T}. \quad (3)$$

The system is extensive, implying that $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$. Therefore it must hold that

$$S = s_1(\rho, n)U + s_2(\rho, n)V + s_3(\rho, n)N, \quad (4)$$

for certain functions $s_{1,2,3}$. Considering dS from (4) and comparing its dU , dV and dN terms with (3), it is seen that $s_1 = 1/T$, $s_2 = p/T$, $s_3 = -\mu/T$, which are functions of ρ and n . These results imply the Euler relation

$$S = \frac{U + pV - \mu N}{T}, \quad (5)$$

or, taken per unit volume,

$$s = \frac{u + p - \mu n}{T}. \quad (6)$$

Consistency between (3) and (5) imposes also

$$dp = \frac{\rho + p - \mu n}{T} dT + n d\mu. \quad (7)$$

Inverting the relation $T = T(\rho, n)$ at fixed n , one obtains $\rho = \rho(T, n)$, which expresses all these quantities as functions of T and n . This allows to derive from (7) the relations

$$\left. \frac{\partial p}{\partial T} \right|_n = \frac{u + p - \mu n}{T} + n \left. \frac{\partial \mu}{\partial T} \right|_n \quad (8)$$

and

$$\left. \frac{\partial p}{\partial n} \right|_T = n \left. \frac{\partial \mu}{\partial n} \right|_T. \quad (9)$$

While n is fixed for cooling a gas in a fixed, closed volume, we can also admit situations where n changes with T , as

it happens when cooling a gas with a movable piston or in the expanding universe. Then we are interested in the total derivative

$$\frac{dp}{dT} = \left. \frac{\partial p}{\partial T} \right|_n + \left. \frac{\partial p}{\partial n} \right|_T \frac{dn}{dT}, \quad (10)$$

and a similar definition for $d\mu/dT$. Combining (8), (9), (6) and (10) we obtain

$$\frac{dp}{dT} = \frac{u + p - n\mu}{T} + n \frac{d\mu}{dT} = s + n \frac{d\mu}{dT}, \quad (11)$$

a result that could also have been obtained directly by dividing (7) by dT . This expresses Eq. (8) for the general case. From (5) we have the thermodynamic relation

$$\mu = \frac{u + p - Ts}{n}. \quad (12)$$

III. EQUILIBRIUM THERMODYNAMICS OF IDEAL QUANTUM GASES

In thermal equilibrium the grand canonical distribution function of an ideal Fermi-Dirac gas with mass m and chemical potential $\mu = \alpha k_B T$ reads for a mode labeled by \mathbf{q} and having energy $E(\mathbf{q})$,

$$\sum_{n_{\mathbf{q}}=0}^1 e^{n_{\mathbf{q}}[\alpha - \beta E(\mathbf{q})]} = 1 + e^{\alpha - \beta E(\mathbf{q})} \quad (13)$$

where $\beta = 1/k_B T$. Accounting for all modes yields

$$\mathcal{Z} = \prod_{\mathbf{q}} \left(1 + e^{\alpha - \beta E(\mathbf{q})} \right) \quad (14)$$

The Fermi-Dirac distribution reads

$$f(\mathbf{q}) = \frac{1}{e^{\beta E(\mathbf{q}) - \alpha} + 1}. \quad (15)$$

We are interested in an ideal gas of particle with mass m and momentum q . Taking periodic boundary conditions for a cube with size $V^{1/3}$, the allowed momenta are $(q_x, q_y, q_z) = 2\pi\hbar V^{-1/3}(n_x, n_y, n_z)$, with integer values of $n_{x,y,z}$, so that

$$E(q) = \sqrt{m^2 c^4 + q^2 c^2}, \quad (16)$$

and

$$\log \mathcal{Z} = V \int \frac{d^3 q}{(2\pi\hbar)^3} \log \left(1 + e^{\alpha - \beta E(q)} \right). \quad (17)$$

From this we derive

$$d \log \mathcal{Z} = \frac{dV}{V} \log \mathcal{Z} + N d\alpha - U d\beta, \quad (18)$$

in which we may identify $U = Vu$ and $N = Vn$ from

$$n = \int \frac{d^3 q}{(2\pi\hbar)^3} f, \quad (19)$$

$$u = \int \frac{d^3 q}{(2\pi\hbar)^3} f E, \quad (20)$$

and conclude that

$$p = nk_B T \log \mathcal{Z}. \quad (21)$$

Reinserting this into (18) we verify the central relation (11). We finally find from (6) that the entropy density equals

$$s = k_B \int \frac{d^3 q}{(2\pi\hbar)^3} [-f \log f - (1-f) \log(1-f)], \quad (22)$$

To derive this result we may use that

$$\beta u - \alpha n = \int \frac{d^3 q f(\beta E - \alpha)}{(2\pi\hbar)^3} = \int \frac{d^3 q}{(2\pi\hbar)^3} f \log \frac{1-f}{f},$$

and

$$\begin{aligned} \beta p &= \int \frac{d^3 q}{(2\pi\hbar)^3} \log(1 + e^{\alpha - \beta E}) \\ &= \int \frac{d^3 q}{(2\pi\hbar)^3} \log \frac{1}{1-f}. \end{aligned} \quad (23)$$

For later use we point out that by inserting $\sum_{i=1}^3 \partial q_i / \partial q_i = 3$ in the first identity and performing a partial integration, we obtain the equivalent results

$$\begin{aligned} p &= -\frac{T}{3} \int \frac{d^3 q}{(2\pi\hbar)^3} \mathbf{q} \cdot \frac{\partial}{\partial \mathbf{q}} \log(1 + e^{\alpha - \beta E}) \\ &= \int \frac{d^3 q}{(2\pi\hbar)^3} f \frac{q^2 c^2}{3E}. \end{aligned} \quad (24)$$

We can also verify from (12) that α takes the equilibrium value

$$\alpha = \beta \mu. \quad (25)$$

For bosons one has the grand canonical partition sum

$$\mathcal{Z} = \prod_{\mathbf{q}} \left(1 - e^{\alpha - \beta E(\mathbf{q})} \right)^{-1}, \quad (26)$$

the Bose-Einstein distribution

$$f(\mathbf{q}) = \frac{1}{e^{\beta E(\mathbf{q}) - \alpha} - 1}, \quad (27)$$

while the entropy reads

$$s = k_B \int \frac{d^3q}{(2\pi\hbar)^3} [-f \log f + (1+f) \log(1+f)]. \quad (28)$$

IV. DECOUPLED QUANTUM MATTER IN THE EXPANDING UNIVERSE

In the expanding universe a certain species may decouple from the other matter, meaning that, given its cross section, the scattering candidates become so sparse that practically no scattering will take place anymore. Then in a flat Friedman metric

$$ds^2 = c^2 dt^2 - a^2(t)(dx^2 + dy^2 + dz^2) \quad (29)$$

the one-particle occupation of the mode with momentum \mathbf{q} satisfies the free-streaming Boltzmann equation [1–3]

$$\partial_t f(q, t) - \frac{\dot{a}}{a} \mathbf{q} \cdot \frac{\partial}{\partial \mathbf{q}} f(q, t) = 0, \quad (30)$$

with right hand side equal to zero (absence of scattering), and a the scale factor of (29). The solution reads

$$f(q, t) = f[a(t)q]. \quad (31)$$

we may connect a temperature to this,

$$T(t) = \frac{\alpha_1 T_1}{a(t)}, \quad \beta(t) = \frac{1}{k_B T(t)}. \quad (32)$$

In the approximation of instantaneous decoupling at temperature T_1 the distribution function reads

$$f(q, t) = \frac{1}{\exp[\beta_1 E(qT_1/T) - \alpha_1] + 1}, \quad (33)$$

where $\beta_1 = 1/k_B T_1$ and $\alpha_1 = \alpha(T_1)$ are *time independent*. For neutrinos the decoupling took place when they were relativistic, $k_B T_1 \gg mc^2$. In that case we $\beta_1 E(qT_1/T) \approx \beta qc$, so f simplifies to

$$f = \frac{1}{e^{\beta pc - \alpha} + 1}, \quad (34)$$

where $\alpha \equiv \alpha_1$ is a constant. Thus even though neutrinos have a mass, their density will be quasi-relativistic, at least as long as their distribution is uniform. (It has been argued that neutrinos are presently condensed on matter concentrations such as galaxy clusters [6].)

It has long been supposed that in this non-equilibrium situation thermodynamics would still apply.

With f from (34) or, more generally from (31), the entropy density (28) is continuous at T_1 and scales as T^3 after that, as does the particle density (19), so that the entropy per particle

$$\sigma = \frac{s(t)}{n(t)} = \frac{s(T_1)}{n(T_1)} \quad (35)$$

is constant, and the entropy in a comoving unit volume $S = N\sigma \sim a^3 s$ conserved. The same holds for the comoving particle number $N \sim a^3 n$.

The energy density is thus simply

$$\begin{aligned} u &= \int \frac{d^3q}{(2\pi\hbar)^3} \frac{E(q)}{e^{\beta qc - \alpha} + 1} \\ &= \left(\frac{k_B T}{2\pi\hbar c} \right)^3 \int \frac{d^3k}{e^{k - \alpha} + 1} E\left(\frac{k_B T k}{c} \right). \end{aligned} \quad (36)$$

The pressure is not taken from (23) but from (24),

$$\begin{aligned} p &= \int \frac{d^3q}{(2\pi\hbar)^3} \frac{1}{e^{\beta qc - \alpha} + 1} \frac{q^2 c^2}{3E(q)} \\ &= \frac{(k_B T)^5}{(2\pi\hbar c)^3} \int \frac{d^3k}{e^{k - \alpha} + 1} \frac{k^2}{E(k_B T k/c)}. \end{aligned} \quad (37)$$

This Ansatz has been adopted because it satisfies the energy conservation

$$\dot{u} + 3 \frac{\dot{a}}{a} (u + p) = 0. \quad (38)$$

Now our point is that this is consistent with thermodynamics when taking $s = n\sigma$ from (28) and μ from (12),

$$\mu = \frac{u + p - Ts}{n} = \left\langle E(q) + \frac{q^2 c^2}{3E(q)} \right\rangle - T\sigma, \quad (39)$$

where the averaging is over expression (33) or (34) for f . For $k_B T \ll mc^2$, where $p/u \approx 0$ it yields $\mu \approx mc^2$, which is consistent with (11) because it cancels the large term $u \approx nmc^2$, thus repairing the relation (1).

In conclusion, thermodynamics does explain the non-equilibrium situation of decoupled quantum matter in the expanding Universe, but the correspondence $\mu = \alpha k_B T$ between the chemical potential μ and α , the time-independent parameter of the Fermi-Dirac distribution (34), is broken and replaced by the general relation (39).

Acknowledgments

The first author was inspired by the crystal clear lectures on statistical physics by the late B. R. A. Nijboer at the University of Utrecht.

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- [1] S. Dodelson, *Modern Cosmology*, (Academic Press, San Diego, 2003), section 2.3.
- [2] S. Weinberg, *Cosmology*, (Oxford University Press, Oxford, U.K., 2008), section 3.1.
- [3] C. Giunti and C. H. Kim, *Fundamentals of neutrino physics and astrophysics*, (Oxford University Press, Oxford, U.K., 2007), section 16.9
- [4] Ref. [1], p. 40, footnote 5.
- [5] L. Leuzzi and Th. M. Nieuwenhuizen, *Thermodynamics of the Glassy State* (Taylor and Francis, London, 2007).
- [6] Th. M. Nieuwenhuizen, *Europhys. Lett.* **86**, 59001 (2009).