An Extended Second Law of Thermodynamics

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The second law of thermodynamics constitutes a fundamental principle of physics, precluding the existence of perpetual motion machines and providing a natural definition of the arrow of time. Its scope extends across virtually all areas of physical theory. Nonetheless, certain systems are known to admit negative absolute temperatures under well-defined conditions, a phenomenon that has been experimentally observed. In this work, we formulate an *extended* version of the first and second laws, which recovers the conventional statement for positive temperatures and extends its applicability to the negative-temperature domain. Illustrative examples are discussed in the contexts of quantum cosmology and Onsager's vortices.

Thermodynamics is related to every field of physics, from classical to quantum to gravitational systems, which postulates standard laws: *i*) *The zeroth law* establishes thermal equilibrium between systems. *ii*) *The first law* indicates the conservation law of energy, which can be expressed as $\mathrm{d}E = T\mathrm{d}S - W$, where E is the total energy, T the temperature, S the entropy and W the work done, that can be related to macroscopic (extensive) parameters such as volume V and (intrinsic) external forces such as pressure P, $W = P\mathrm{d}V + ...$ *iii*) *The second law* dictates that the change of entropy, for an isolated system, is always equal to zero or increases, i.e., $\mathrm{d}S \geq 0$, and thus a time arrow is defined. *iv*) *The third law* prohibits a system from reaching an absolute temperature equal to zero.

Although these laws are (empirically) fundamental in physics and are obeyed by most systems, there exist some systems where the standard second law (SSL) fails; in these examples, a particular effect is observed: they admit negative absolute temperatures (NAT) [1–5]. We can ask whether for negative absolute temperatures the standard laws of thermodynamics are fulfilled, or whether we need to change or complete them. In particular, this article focuses on the second law.

To delve deeper into this law, we use the definition of temperature, which is related to entropy and goes beyond kinetic energy. In particular, we use the Boltzmann definition, but it is not unique (for example, the Gibbs temperature [6])

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_X , \tag{1}$$

where $(\ \ )_X$ indicates that for partial differentiation, the variables in the first law X should be constant. The fact that a Hamiltonian depends on quadratic terms implies that the SSL is valid. However, with this definition for the temperature (1), we can obtain NAT systems.

Negative absolute temperature has been observed in systems where the phase space is bounded. Here, a threshold energy E^* can be obtained due to the phase space volume being finite and the additional energy to a system allowing it to explore wider regions of the phase space. We can get three scenarios: *i*) for $E < E^*$, $T > 0$; *ii*) for $E = E^*$, $T \to \pm\infty$; and *iii*) for $E < E^*$, $T < 0$. This behavior is found not only for bounded phase-space systems, but also for the discrete non-linear Schrödinger equation [7, 8].

A counterintuitive statement is the fact that the negative absolute temperature is "hotter" than the positive absolute temperature. This is because, when a system with $T < 0$ and a system with $T > 0$ interact, the final result of the thermal equilibrium of the total system goes to a positive temperature. Therefore, the common temperature in nature is positive. To obtain systems with negative absolute temperature, it is necessary to work with perfectly isolated systems with other systems with positive absolute temperature. The change of sign in temperature can be interpreted as a phase transition (See more details in [1–3, 9]).

Here we put forward an *extended* second law (ESL) of thermodynamics that is valid also for NAT systems, which can be read as

$$\mathrm{sign}(T)\,\mathrm{d}S \geq 0, \tag{2}$$

this new form of the second law of thermodynamics includes the SSL when $T > 0$, that is the usual case in physics, and extends the regimen of validity when the system admits $T < 0$. This ESL can be applied to different cases where the SSL is violated when $T < 0$, for instance, the Onsager's vortices [4, 10, 11], incompressible fluids [12], nuclear magnetic chains [13–17], lasers [18], cold atoms [19–21], optical waveguides [22], and quantum cosmology [5]. Some of these examples have experimentally confirmed the negative absolute temperature and $\mathrm{d}S < 0$ in the same regime. An interpretation of

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this sign change for the temperature is as a phase transition. We will apply the ESL to a model in loop quantum cosmology, as well as the Onsager's vortices to show the consistency within these examples.

I. LOOP QUANTUM COSMOLOGY

Loop Quantum Cosmology (LQC) is the application of techniques in Loop Quantum Gravity (LQG) [23, 24] to a cosmological model, in particular, isotropic, homogeneous, and flat universe [25–27]. Loop quantization replaces the classical Big Bang singularity with a quantum bounce [26–31]. We can explore the thermodynamics for this model in LQC (See more details in [5, 32–34]). When we focus on the generalized second law (GSL), that is, the sum of all contributions of entropy, the gravitational S_g and matter S_m parts, makes use of both the logarithmic correction to gravitational entropy and the weak condition of energy for the matter part ($P+\rho \geq 0$ and $\rho \geq 0$). Therefore, the change of entropy with respect to cosmic time is written as

$$\dot{S}_g = -2\pi \frac{\dot{H}}{H^3}(1+\alpha H^2), \tag{3}$$

$$\begin{aligned} \dot{S}_m &= -\frac{4\pi(P+\rho)}{TH^4}\left(H^2+\dot{H}\right), \\ &= 4\pi \frac{\dot{H}}{H^3}\frac{\dot{H}+H^2}{\left(2H^2+\dot{H}\right)}\left(\frac{\rho_c}{\rho_c-2\rho}\right), \end{aligned} \tag{4}$$

where P is the pressure, ρ is the energy density, and α is the parameter due to the logarithmic correction in the gravitational entropy $S_g = A_A/4 + \pi\alpha \ln(A_A/4) + \beta$ [35–39], A_A is the apparent area [5, 40–43], and H is the Hubble parameter for the effective model in LQC

$$H^2 = \frac{8\pi}{3}\rho\left(1-\frac{\rho}{\rho_c}\right), \tag{5}$$

here, ρ_c is the critical density mass, when $\rho = \rho_c$ the quantum bounce happens. In addition, $\dot{H}$ changes the sign at $\rho = \rho_c/2$ because we have [26, 27]

$$\dot{H} = -4\pi(P+\rho)\left(1-\frac{2\rho}{\rho_c}\right). \tag{6}$$

The threshold energy occurs when $\dot{H}+2H^2$ changes sign. Furthermore, the temperature T in the gravitational case is associated with the gravity surface κ

$$T = \frac{\kappa}{2\pi}, \tag{7}$$

the surface gravity at the apparent horizon of this cosmic model is given by

$$\begin{aligned} \kappa &= -\frac{R_A}{2}\left(\dot{H}+2H^2\right), \\ &= -\frac{1}{R_A}\left(1-\frac{\dot{R}_A}{2HR_A}\right), \end{aligned} \tag{8}$$

where R_A is the apparent radius of the cosmic horizon [5, 40–43]. Note that $T > 0$ when $\dot{H}+2H^2 < 0$, and $T < 0$ when $\dot{H}+2H^2 > 0$. This is possible since $\dot{H} < 0$ for the region $0 < \rho < \frac{\rho_c}{2}$ and $\dot{H} > 0$ for $\frac{\rho_c}{2} < \rho < \rho_c$.
The standard analysis of the second law in cosmology does not include the possibility of NAT, where the GSL is violated close to the quantum bounce in almost all cases (See more details in [5, 32]). Nevertheless, we can observe that the LQC phase space is effectively bounded. Thus, the threshold energy is located at $\dot{H}+2H^2$, and the Universe is an example of a perfectly isolated system. Thus, the effective LQC model can, in principle, admit negative absolute temperatures.
The novel result here is the application of the *extended generalized second law* (EGSL) in LQC, particularly in the region close to the quantum bounce ($\frac{\rho_c}{2} < \rho < \rho_c$), where the GSL is violated. Since this system admits NAT and the ESL is written as in (2), the validity domain of the second law of thermodynamics can be extended in LQC not only for the cases where $T > 0$ holds, but also for the cases where NAT is present. This sign change of the temperature can be interpreted as a phase transition for the Universe when $\dot{H}+2H^2$ also changes sign. In what follows, we shall consider another physical system that exhibits non-standard properties regarding the expected thermodynamic behavior.

II. ONSAGER'S VORTICES

The Onsager vortices [4] introduced the idea of having NAT systems, where the Euler equation describes the time evolution of a two-dimensional incompressible ideal flow $\mathbf{u}$, which is bounded in a domain with an area A

$$\begin{aligned} &\partial_t \mathbf{u} + (\mathbf{u}\cdot\nabla)\mathbf{u} = -\frac{\nabla P}{\rho}, \\ &\nabla\cdot\mathbf{u} = 0, \end{aligned} \tag{9}$$

here, ρ and P are constant density and pressure of the fluid. The vorticity w can be defined in a perpendicular unitary direction $\hat{\mathbf{k}}$ to the plane of the flow as follows

$$\nabla\times\mathbf{u} = w\hat{\mathbf{k}}, \tag{10}$$

the vorticity can contain N point-vortices at any time, each one of them with circulation Γ_i

$$w(\mathbf{r},t) = \sum_{i=1}^{N}\Gamma_i\delta\left(\mathbf{r}-\mathbf{r}_i(t)\right), \tag{11}$$

it is possible to build the corresponding Hamiltonian

$$\mathcal{H}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\right) = \sum_{i\neq j}\Gamma_i\Gamma_j\mathcal{G}\left(\mathbf{r}_i,\mathbf{r}_j\right) \tag{12}$$

where $\mathcal{G}\left(\mathbf{r}_i,\mathbf{r}_j\right)$ is the Green's function. Since the N vortices are in a bounded area A, the phase space is enclosed

by a constant energy hypersurface E.
Entropy of this system is calculated using the density of states $\omega(E)$

$$S(E) = k_B \ln \omega(E), \tag{13}$$

where k_B is the Boltzmann constant. Furthermore, the density approaches zero when $E \to \pm\infty$. There exists a maximum finite value E_M, where the entropy decreases to obtain NAT at $E > E_M$. In this case, the ESL can also be applied to extend the validity domain because the SSL is violated in this region.
This line of investigation has been addressed in many articles using analytical [2–4], numerical [10–12], and experimental [44, 45] methods, in which the NAT and SSL violations have been confirmed.

III. CONCLUSIONS

The second law of thermodynamics is generally valid for systems at positive absolute temperature. However, it is natural to ask whether this standard second law remains applicable in situations where a system admits a negative absolute temperature. Such systems, studied across various areas of physics, display unconventional thermodynamic behavior and, in some cases, have been observed to violate the SSL.

We have reviewed the conditions under which NAT can occur, following earlier foundational work [1–3]. These conditions include the assignment of a temperature to each thermodynamic state, the existence of a bounded phase space, and the isolation of the system from others at positive temperature.

In this manuscript, we have proposed an extension of the second law of thermodynamics, which reproduces the standard second law for $T > 0$ and remains valid for systems with $T < 0$. This extended formulation is expressed in Eq. (2). We have illustrated its applicability with two representative examples exhibiting negative absolute temperature, showing that the extended second law enlarges the domain of validity compared to the SSL. In both cases, the systems satisfy the NAT conditions: they are isolated and possess a bounded phase space that leads to the existence of a threshold energy.

As a direction for future research, the ESL may be tested in a broader class of systems exhibiting NAT, where the SSL fails to account for this apparent "paradoxical" thermodynamic behavior [4, 5, 10–22].

While the interpretation of negative temperature remains unsettled, we expect that this formulation will contribute to a clearer understanding of its thermodynamic role and stimulate further investigations.

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