Fluctuation theorem for entropy production during effusion of a relativistic ideal gas

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The probability distribution of the entropy production for the effusion of a relativistic ideal gas is calculated explicitly. This result is then extended to include particle and antiparticle pair production and annihilation. In both cases, the fluctuation theorem is verified.

I. INTRODUCTION

The fluctuation theorem [1] can be seen as a natural extension to far from equilibrium situations of the pioneering work of Onsager on the reciprocity relations. The theorem has been proven in a variety of settings, including thermostated systems [2], Markov processes [3], classical Hamiltonian dynamics [4,5], quantum dynamics, quantum field theory [6], and relativity [7]. The wide range of validity of the theorem reflects the fact that it derives from two basic ingredients of the fundamental laws of nature: time reversibility and time translational invariance. The effusion of gases provides a simple setting in which the fluctuation theorem can be verified on the basis of freshmen's physics [8,9]. The effusion of radiation (photons) can be discussed on a similar basis [10]. In this paper, we show that the fluctuation theorem is also valid for the effusion of classical relativistic particles, including particle and antiparticle pair production and annihilation.

II. FLUCTUATION THEOREM FOR EFFUSION OF A RELATIVISTIC IDEAL GAS

Two relativistic ideal gases A and B are initially in equilibrium in containers at given densities ρ_i and temperature T_i, $i \in \{A, B\}$ while separated by a common adiabatic wall [11]. At time $t=0$, a small hole with surface area σ is opened, allowing an exchange of particles and energy between the two gases during a (fixed) time interval of length t. We assume the presence of an energy filter, so that only particles with total energy in the range $[E_1, E_2]$ can cross. The dimensions of the hole are supposed to be small compared to the mean free path of the gas particles, and the reservoirs sufficiently large so that the equilibrium state in both parts is not affected by the exchange. In particular, the temperatures and densities in both reservoirs remain constant. Hence, the change in entropy in the total system, upon a total transfer of energy ΔU and of particles ΔN from A to B during t, is given by

$$\Delta S = -\frac{1}{T_A}\Delta U + \frac{\mu_A}{T_A}\Delta N + \frac{1}{T_B}\Delta U - \frac{\mu_B}{T_B}\Delta N$$
$$= \mathcal{A}_U \Delta U + \mathcal{A}_N \Delta N. \tag{1}$$

We introduced, in accordance with the definitions from irreversible thermodynamics, the following thermodynamic

forces (affinities) for energy and particle flow:

$$\mathcal{A}_U = \frac{1}{T_B} - \frac{1}{T_A},$$

$$\mathcal{A}_N = \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} = k \ln\left[\frac{\rho_A T_B K_2(mc^2/kT_B)}{\rho_B T_A K_2(mc^2/kT_A)}\right], \tag{2}$$

with K_2 a modified Bessel function of the second kind. The expression for the chemical potential reads

$$\mu = -kT \ln\left(\frac{4\pi(mc)^3}{\rho h^3}\frac{K_2(mc^2/kT)}{mc^2/kT}\right). \tag{3}$$

We use the convention that the internal energy U of the gas comprises both the kinetic energy and the rest energy of the particles (mc^2). Note that the thermodynamic force $\mathcal{A}_N$ diverges when one of the (infinitely large) reservoirs is empty, so that free effusion into unlimited space, implying an infinitely large entropy production, corresponds to a singular limit.

We will show below that the joint probability density $P_t(\Delta U, \Delta N)$ satisfies the following detailed fluctuation theorem:

$$\frac{P_t(\Delta U, \Delta N)}{P_t(-\Delta U, -\Delta N)} = e^{\Delta S/k}, \tag{4}$$

with ΔS given by Eq. (1). This encompasses as a special case the more familiar form of the fluctuation theorem $P_t(\Delta S)/P_t(-\Delta S) = \exp\{\Delta S/k\}$. Since the increments of ΔU and ΔN in successive time intervals are independent, one has that

$$\langle e^{-(\lambda_U \Delta U + \lambda_N \Delta N)} \rangle = e^{-tQ(\lambda_U, \lambda_N)}, \tag{5}$$

where $Q(\lambda_U, \lambda_N)$ is the cumulant generating function. In terms of the latter, the detailed fluctuation theorem reads

$$Q(\lambda_U, \lambda_N) = Q(\mathcal{A}_U/k - \lambda_U, \mathcal{A}_N/k - \lambda_N). \tag{6}$$

III. MASTER EQUATION AND CUMULANT GENERATING FUNCTION

During a small time interval dt, the contributions to the

quantities ΔU and ΔN result from individual particle transport across the hole. The corresponding transition rate $T_{i \to j}(E)$ to observe a particle with energy E crossing the hole from $i \to j$ is given by

$$T_{i \to j}(E) = \frac{\sigma \rho_i}{4c^2(mc)^3} \frac{(mc^2/kT_i)e^{-E/kT_i}}{K_2(mc^2/kT_i)} (E^2 - m^2c^4). \quad (7)$$

The derivation of this result is similar to the nonrelativistic case [8], but with the velocities described by the Jüttner distribution [12]. The probability density $P_t(\Delta U, \Delta N)$ then obeys the following master equation:

$$\frac{\partial}{\partial t} P_t(\Delta U, \Delta N) = \int_{E_1}^{E_2} T_{A \to B}(E) P_t(\Delta U - E, \Delta N - 1) dE$$

$$+ \int_{E_1}^{E_2} T_{B \to A}(E) P_t(\Delta U + E, \Delta N + 1) dE$$

$$- P_t(\Delta U, \Delta N) \int_{E_1}^{E_2} [T_{A \to B}(E) + T_{B \to A}(E)] dE, \quad (8)$$

subject to the initial condition $P_0(\Delta U, \Delta N) = \delta(\Delta U)\delta_{\Delta N,0}$. Multiplying the master equation with $\exp\{-\lambda_U \Delta U - \lambda_N \Delta N\}$ and subsequent integration over ΔU and summation over ΔN leads to the following analytical result:

$$Q(\lambda_U, \lambda_N) = I_A(0,0) - I_A(\lambda_U, \lambda_N) + I_B(0,0) - I_B(-\lambda_U, -\lambda_N), \quad (9)$$

where we define

$$I_i(\lambda_U, \lambda_N) = \int_{E_1}^{E_2} T_{i \to j}(E) e^{-\lambda_U E - \lambda_N} dE$$

$$= \frac{e^{-\lambda_N}\sigma\rho_i}{4m^2c^3} \frac{(kT_i)^2(1 + \lambda_U kT_i)^{-3}}{K_2(mc^2/kT_i)}$$

$$\times \Big[e^{-(1/kT_i + \lambda_U)E_1}\{2 + 2E_1(kT_i)^{-1} + \lambda_U$$

$$+ (E_1^2 - m^2c^4)((kT_i)^{-1} + \lambda_U)^2\}$$

$$- e^{-(1/kT_i + \lambda_U)E_2}\{2 + 2E_2(kT_i)^{-1} + \lambda_U$$

$$+ (E_2^2 - m^2c^4)((kT_i)^{-1} + \lambda_U)^2\}\Big]. \quad (10)$$

Equation (9), together with Eq. (10), is the central result of this paper. A tedious calculation, using the explicit expressions for the thermodynamic forces given in Eq. (2), reveals that this expression indeed verifies the detailed fluctuation theorem Eq. (6).

IV. CUMULANTS

A Taylor expansion of the cumulant generating function gives immediately the expressions of the joint cumulants κ_{ij} (of power i in the energy flux and power j in the particle flux):

$$Q(\lambda_U, \lambda_N) = -\frac{1}{t} \sum_{i,j} \frac{(-1)^{i+j} \lambda_U^i \lambda_N^j}{i!j!} \kappa_{ij}. \quad (11)$$

As the higher order expressions quickly become unwieldy, we will only present the first order results, namely, $\kappa_{10} = \langle \Delta U \rangle$ and $\kappa_{01} = \langle \Delta N \rangle$. These results will be used in the next section to validate the Onsager symmetry:

$$\langle \Delta U \rangle = \frac{t\sigma\rho_A}{4m^2c^3 K_2(mc^2/kT_A)} \{ e^{-E_1/kT_A}[E_1^3 - E_1 m^2c^4 + 3E_1^2 kT_A - m^2c^4 kT_A + 6E_1(kT_A)^2 + 6(kT_A)^3]$$

$$- e^{-E_2/kT_A}[E_2^3 - E_2 m^2c^4 + 3E_2^2 kT_A - m^2c^4 kT_A + 6E_2(kT_A)^2 + 6(kT_A)^3]\} - \frac{t\sigma\rho_B}{4m^2c^3 K_2(mc^2/kT_B)} \{ e^{-E_1/kT_B}[6(kT_B)^3 - E_1 m^2c^4$$

$$+ 3E_1^2 kT_B - m^2c^4 kT_B + 6E_1(kT_B)^2 + E_1^3] - e^{-E_2/kT_B}[6(kT_B)^3 - E_2 m^2c^4 + 3E_2^2 kT_B - m^2c^4 kT_B + 6E_2(kT_B)^2 + E_2^3]\}, \quad (12)$$

$$\langle \Delta N \rangle = \frac{t\sigma\rho_A}{4m^2c^3 K_2(mc^2/kT_A)} \{ e^{-E_1/kT_A}[E_1^2 - m^2c^4 + 2E_1 kT_A + 2(kT_A)^2] - e^{-E_2/kT_A}[E_2^2 - m^2c^4 + 2E_2 kT_A + 2(kT_A)^2]\}$$

$$- \frac{t\sigma\rho_B}{4m^2c^3 K_2(mc^2/kT_B)} \{ e^{-E_1/kT_B}[E_1^2 - m^2c^4 + 2E_1 kT_B + 2(kT_B)^2] - e^{-E_2/kT_B}[E_2^2 - m^2c^4 + 2E_2 kT_B + 2(kT_B)^2]\}. \quad (13)$$

Both $\langle \Delta U \rangle$ and $\langle \Delta N \rangle$ grow linear in time, in accordance with the fact that their increments are independent.

V. ONSAGER RELATION

The average entropy production during the effusion process is obtained by averaging Eq. (1) and taking the time derivative

$$\frac{d}{dt}\langle \Delta S\rangle = \mathcal{A}_U \mathcal{J}_U + \mathcal{A}_N \mathcal{J}_N, \tag{14}$$

where we introduce the macroscopic fluxes $\mathcal{J}_U = \frac{d}{dt}\langle \Delta U\rangle$ and $\mathcal{J}_N = \frac{d}{dt}\langle \Delta N\rangle$ corresponding to energy and particle transport. These fluxes in general depend nonlinearly on the thermodynamic forces. Close to equilibrium, when the thermodynamic forces are small (that is, for small temperature and density difference), the expressions can be linearized, and written in compact matrix notation $\bar{\mathcal{J}} = L\bar{\mathcal{A}}$ using $\bar{\mathcal{J}} = (\mathcal{J}_U, \mathcal{J}_N)^T$, $\bar{\mathcal{A}} = (\mathcal{A}_U, \mathcal{A}_N)^T$ and the Onsager matrix L. The explicit expression for the Onsager coefficients L_{ij} are obtained from Eqs. (12) and (13)

$$L_{UU} = \frac{\sigma\rho}{4km^2c^3K_2(mc^2/kT)}$$
$$\times \{e^{-E_1/kT}[E_1^4 + 4E_1^3kT + 12E_1^2(kT)^2 - E_1^2m^2c^4$$
$$+ 24E_1(kT)^3 - 2E_1kTm^2c^4 + 24(kT)^4 - 2k^2T^2m^2c^4]$$
$$- e^{-E_2/kT}[E_2^4 + 4E_2^3kT + 12E_2^2(kT)^2 - E_2^2m^2c^4$$
$$+ 24E_2(kT)^3 - 2E_2kTm^2c^4 + 24(kT)^4 - 2k^2T^2m^2c^4]\};$$

$$L_{UN} = L_{NU} = \frac{\sigma\rho}{4km^2c^3K_2(mc^2/kT)}$$
$$\times \{e^{-E_1/kT}[E_1^3 + 3E_1^2kT + 6E_1(kT)^2$$
$$- E_1m^2c^4 + 6(kT)^3 - kTm^2c^4]$$
$$- e^{-E_2/kT}[E_2^3 + 3E_2^2kT + 6E_2(kT)^2$$
$$- E_2m^2c^4 + 6(kT)^3 - kTm^2c^4]\};$$

$$L_{NN} = \frac{\sigma\rho}{4km^2c^3K_2\left(\frac{mc^2}{kT}\right)}\{e^{-E_1/kT}[E_1^2 + 2E_1kT + 2(kT)^2 - mc^2]$$
$$- e^{-E_2/kT}[E_2^2 + 2E_2kT + 2(kT)^2 - mc^2]\}. \tag{15}$$

The symmetry property of the matrix is a direct consequence of the symmetry relation Eq. (6) of the cumulant generating function.

These expressions significantly simplify when considering an infinitesimal energy window $E_1 = E_0 - dE/2$ and $E_2 = E_0 + dE/2$ ($dE \ll E_0$). In this case, there is a strong coupling between the particle and energy current: every particle that crosses carries a energy E_0 and so $\mathcal{J}_U = E_0\mathcal{J}_N$. This is reflected in the Onsager matrix, after expanding the L_{ij} to first order in dE:

$$L_{UU} = E_0^2 L_{NN}, \quad L_{UN}(=L_{NU}) = E_0 L_{NN},$$

$$L_{NN} = \frac{\sigma\rho(E_0^2 - m^2c^4)e^{-E_0/kT}dE}{4km^2c^3K_2(mc^2/kT)}. \tag{16}$$

The determinant of the Onsager matrix is identically zero, as both rows are linear dependent. This opens up the possiblity, in principle, to use the system as a thermodynamic engine attaining Carnot or Curzon-Ahlborn efficiencies [13,14].

VI. PAIR PRODUCTION

One important aspect of relativistic gases, which we have not considered so far, is the production and annihilation of particle-antiparticle pairs [15]. This must be included in a consistent treatment of relativistic effusion by considering the corresponding exchange of antiparticles between the two compartments.

In our framework, in which both reservoirs independently are (and remain) in equilibrium, this implies the existence of a second ideal gas in each reservoir consisting of antiparticles. Because of the production and annihilation, both particles and antiparticles will be created and destroyed. This process can be represented by a chemical reaction of the form $x + \bar{x} \rightleftharpoons 0$ (x represents a particle, $\bar{x}$ the corresponding antiparticle). Equilibrium is achieved when the two chemical potentials (μ and $\bar{\mu}$) satisfy $\mu + \bar{\mu} = 0$. For a given temperature this relation determines the density $\bar{\rho}$ of the antiparticles. Using Eq. (3) gives

$$\bar{\rho} = \left[4\pi\left(\frac{mc}{h}\right)^3\frac{K_2(mc^2/kT)}{mc^2/kT}\right]^2\frac{1}{\rho}. \tag{17}$$

Note that fluctuations of (anti)particles' number and energy around their equilibrium values can be neglected, as both reservoirs are assumed to be infinitely large.

The exchange of antiparticles through the opening between volumes A and B will contribute to the entropy change ΔS. Since the chemical potential of the antiparticles is just the negative of the chemical potential of the particles we find instead of Eq. (1)

$$\Delta S = \mathcal{A}_U \Delta U + \mathcal{A}_N(\Delta N - \Delta\bar{N}), \tag{18}$$

with $\mathcal{A}_U$ and $\mathcal{A}_N$ given by Eq. (2). To account for the fluctuations in ΔS due to the exchange of antiparticles the joint probability distribution has to be augmented to $P(\Delta U, \Delta N, \Delta\bar{N})$, and its time evolution is now governed by the master equation

$$\frac{\partial}{\partial t}P_t(\Delta U, \Delta N, \Delta\bar{N}) = \int_{E_1}^{E_2}[T_{A\to B}(E)P_t(\Delta U - E, \Delta N - 1, \Delta\bar{N})$$
$$+ \bar{T}_{A\to B}(E)P_t(\Delta U - E, \Delta N, \Delta\bar{N} - 1)$$
$$+ T_{B\to A}(E)P_t(\Delta U + E, \Delta N + 1, \Delta\bar{N})$$
$$+ \bar{T}_{B\to A}(E)P_t(\Delta U + E, \Delta N, \Delta\bar{N} + 1)]dE$$
$$- P_t(\Delta U, \Delta N, \Delta\bar{N})\int_{E_1}^{E_2}[T_{A\to B}(E)$$
$$+ \bar{T}_{A\to B}(E) + T_{B\to A}(E) + \bar{T}_{B\to A}(E)]dE, \tag{19}$$

where the rates $T_{i \to j}(E)$ and $\bar{T}_{i \to j}(E)$ are defined by Eq. (7) with ρ_i replaced by $\bar{\rho}_i$ in the latter case. The corresponding cumulant generating function is given by

$$\langle e^{-(\lambda_U \Delta U + \lambda_N \Delta N + \lambda_{\bar{N}} \Delta \bar{N})} \rangle = e^{-tQ(\lambda_U, \lambda_N, \lambda_{\bar{N}})}. \tag{20}$$

The detailed fluctuation theorem acquires the form

$$Q(\lambda_U, \lambda_N, \lambda_{\bar{N}}) = Q(\mathcal{A}_U/k - \lambda_U, \mathcal{A}_N/k - \lambda_N, \mathcal{A}_{\bar{N}}/k - \lambda_{\bar{N}}). \tag{21}$$

Similar to Eq. (9) we now find

$$\begin{aligned}
Q(\lambda_U, \lambda_N, \lambda_{\bar{N}}) = {} & I_A(0,0) - I_A(\lambda_U, \lambda_N) + \bar{I}_A(0,0) - \bar{I}_A(\lambda_U, \lambda_{\bar{N}}) \\
& + I_B(0,0) - I_B(-\lambda_U, -\lambda_N) \\
& + \bar{I}_B(0,0) - \bar{I}_B(-\lambda_U, -\lambda_{\bar{N}}),
\end{aligned} \tag{22}$$

with $I_i(\lambda_U, \lambda_N)$ given by Eq. (10). For $\bar{I}_i$ the density is $\bar{\rho}_i$. Using these expressions in Eq. (22) it is again straightforward to verify Eq. (21). The inclusion of pair production thus opens an additional channel for entropy production. However, due to the equilibrium relations between the chemical potentials of particles and antiparticles ($\mu + \bar{\mu} = 0$) and their respective concentrations [Eq. (17)] the fluctuation theorem remains valid.

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