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Entropy: A Review

S. R. G. Trevisani*

Universidade de São Paulo, Department of Astronomy (IAGUSP) Matão Street, Brazil

***Corresponding Author:** S. R. G. Trevisani, Universidade de São Paulo, Department of Astronomy (IAGUSP) Matão Street, Brazil.

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Although the concept of entropy is one of the most important in physics your complete understanding seems to remain incomplete. This paper was written with the aim of addressing some of the issues concerning entropy in the (non-relativistic) formalism of the statistical mechanics and the (general relativistic) kinetic theory.

Introduction

Second Law of Thermodynamics

"Every thermal machine carrying out continuous cycles must operate between two thermal sources: one hot and one cold. The machine cannot convert the heat received from the hot source entirely into work. part of this heat is transformed into work and the remainder is inevitably transferred to the cold source" [1].

Although it is possible to fully convert work into heat in a reversible thermodynamic system, the opposite is not true. If the entire Universe were at the same temperature, it would not be possible to convert any of its heat energy into work.

The Clausius theorem configures the reversibility potential of thermodynamic systems

$$\oint_C \frac{dQ}{T} = 0 \quad \text{(Reversible Processes)} \quad (1)$$

$$\oint_C \frac{dQ}{T} \leq 0 \quad \text{(Irreversible Processes)} \quad (2)$$

It follows from this theorem that the first integral above has the same null value for all reversible paths that connect the initial and final states of thermodynamic equilibrium.

The most important consequence of the Clausius theorem is the possibility of defining a new state function associated with the thermodynamic equilibrium of a system, the Entropy S:

$$\int_{\mathrm{a}}^{\mathrm{b}} \frac{dQ}{T} \equiv (-S_{\mathrm{b}}) - (-S_{\mathrm{a}}) \equiv \Delta S\,. \qquad (3)$$

As the final entropy of some thermal system that tends to equilibrium is always smaller - inequality (2) - than

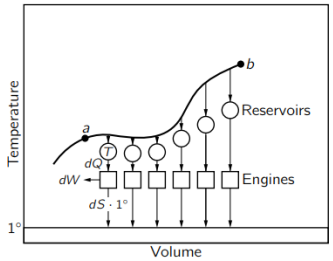

Figure 1: Diagram Showing the Relationship Between T and V for a Reversible Thermodynamic System in Terms of Infinitesimal Steps in Volume

the initial entropy of the system (ENTROPY INCREASE PRINCIPLE) we have to

$$\Delta S \geq 0 .$$

The value ΔS = 0 corresponds, for example, to the Carnot Engine: a structure with the highest possible efficiency that carries out thermodynamic cycles.

Boltzmann and the "2nd Law"

It is possible to establish a complete analogy between the evolution of the probability of macrostates of a system in the direction of equilibrium and the principle of increasing entropy, which leads us to infer that entropy must be a measure associated with thermodynamic probability [2].

If we associate a statistical weight Ω with a macrostate defined as the number of compatible microstates, the entropy must therefore be an increasing function of Ω.

What kind of increasing function this should be is suggested when we consider the concept that entropy is an additive quantity.

On the other hand, the probability Ω associated with a macrostate of a system is the product of the probabilities of the microstates of the components

$$\Omega = \Omega 1\ \Omega 2 \rightarrow S = S1 + S2 .$$

A function with the property of taking products into sums is logarithmic. In these terms we are led to the famous general result due to Max Planck

$$S = k \ln\Omega \quad (4)$$

where k corresponds to some constant.

Application

Consider two thermodynamic systems 1 and 2 initially thermally isolated from each other, with respective initial internal energies ($\rho_1^{(0)}$) and ($\rho_2^{(0)}$). If the two systems are subsequently subjected to thermal contact, then they can exchange heat (energy) freely, which configures a state of greater probability. in this contact condition the two systems must be at the same thermodynamic temperature

$$\beta_1 = \beta_2 \equiv \bar{\beta} \equiv \frac{1}{k\bar{T}} .$$

(The T corresponds to the temperature of maximum probability ("bar" state kept in contact the two systems)).

It follows from conservation of energy that

$$\bar{\rho}_1 + \bar{\rho}_2 = \rho_1^{(0)} + \rho_2^{(0)}$$

Define the quantities

$$\chi_1 \equiv \bar{\rho}_1 - \rho_1^{(0)} \quad \text{and} \quad \chi_2 \equiv \bar{\rho}_2 - \rho_2^{(0)} .$$

In this term

$$\chi_1 + \chi_2 = 0 .$$

Consider that the systems 1 and 2 are effectively subjected to thermal contact corresponds to an energetic evolution such that

$$\Omega(\bar{\rho}) > \Omega(\rho^{(0)}) \geq 0$$

where Ω(ρ) corresponds to the probability of being in a macrostate with energy ρ.

Implementing the property of the logarithm of monotonic functions

$$\Omega_1(\bar{\rho}_1)\Omega_2(\bar{\rho}_2) > \Omega_1(\rho_1^{(0)})\Omega_2(\rho_2^{(0)}) \geq 0$$

$$\Rightarrow \ln\Omega_1(\bar{\rho}_1) + \ln\Omega_2(\bar{\rho}_2) > \ln\Omega_1(\bar{\rho}_1^{(0)}) + \ln\Omega_2(\bar{\rho}_2^{(0)}) \geq 0$$

Expanding the term to the right of the previous inequality in a Taylor series

$$\left.\frac{\partial \ln\Omega_1}{\partial\rho}\right|_{\rho_1^{(0)}} (\bar{\rho}_1 - \rho_1^{(0)}) + \left.\frac{\partial \ln\Omega_2}{\partial\rho}\right|_{\rho_2^{(0)}} (\bar{\rho}_2 - \rho_2^{(0)}) \geq 0\,.$$

Implementing the previously defined quantity χ and identifying

$$\beta \equiv \frac{\partial \ln\Omega}{\partial\rho} \equiv \frac{1}{kT}\,,$$

then

$$\Rightarrow \frac{\chi_1}{T_1^{(0)}} - \frac{\chi_2}{T_2^{(0)}} \geq 0 = \Delta s$$

where $s \equiv S/V.$

General Relativity

From now on, in order to simplify matters we assume a flat FLRW geometry

$$ds^2 = dt^2 - a^2(t)\left(dx^2 + dy^2 + dz^2\right), \qquad (5)$$

for which is well know that the non-nulls Christoffel symbols $\Gamma^{\lambda}_{\mu\nu}$ related to the representation of the curvature of this space-time description are

$$\Gamma^i_{0j} = \frac{\dot{a}}{a}\delta^i_j \equiv H\delta^i_j \quad \text{and} \quad \Gamma^0_{ij} = -\frac{\dot{a}}{a}g_{ij} \equiv -Hg_{ij}\,, \quad (6)$$

where a "overdot" means time derivative and (H) is called the Hubble Parameter.

Relativistic Standard Kinetic Theory

The Relativistic Boltzmann Equation

In this context, the BE under the influence of a gravitational field (geodesic equation in the flat FLRW geometry) in terms of

$$p^2 \equiv g_{ij}P^iP^j \;\Rightarrow\; p = \left(g_{ij}P^iP^j\right)^{1/2}$$

and respecting the "mass shell" condition

$$p^2 \equiv E^2 - m^2 \;\Rightarrow\; \frac{\partial f}{\partial P^0} = 0$$

is described as

$$L(f) = \frac{df}{d\lambda} = P^0\left(\frac{\partial f}{\partial t} - Hp\frac{\partial f}{\partial p}\right) \equiv C(E)$$

The C(E) term corresponds to some (kinetical) to be modeled considering the phenomenological regime in action.

The Standard Kinetic Term C(E)

Consider the description of the interactions between the elements of the system made (exclusively and) completely in terms of the following model: a beam of particles with physical momentum P∗i incident on another beam of particles with physical momentum Pi.

Defining

- $\Gamma \equiv \Gamma(t, X^i, P^i, P^i_*, dV_*)$as phase space such that elements of its components that interact (collide) abandon it: the integral of the product N(t) × N∗(t) ≡ ΔN− indicates the modulus of this variation.

$$\Delta N^- = \int\int_{(3)P_*} (ff_*)\,\mathbf{V}^-[d^3X, d^3P, dV_*]d^3P_*\Delta t \quad (7)$$

- $\Gamma' \equiv \Gamma'(t', x^{i'}, P^{i'}, P^{i'}_*, dV_*{}')$ as the phase space such that elements and their components that interact (collide) come to compose the Γ defined earlier: the integral of $N'(t) \times N'_*(t) \equiv \Delta N^+$, in turn, quantifies the totality of this variation

$$\Delta N^{+} = \int \int_{(3)P_{*}^{'}} (f^{'} f_{*}^{'})\, \mathbf{V}^{+}[d^{3}X^{'}, d^{3}P^{'}, dV_{*}^{'}] d^{3}P_{*}^{'} \Delta t^{'} \tag{8}$$

It was adopted in this description V ± as representing an arbitrary geometric element that represents the subspace containing the particles after they collide.

The "Liouville Theorem" ensures that " following the motion of volumes occupied by sets of points in arbitrary phase spaces, the moduli of these volumes remain unchanged over time, although they constantly change their shape", that is

$$\int \mathbf{V}^{-}(d^{3}X, d^{3}P, dV_{*}) d^{3}P_{*} \Delta t = \\ = \int \mathbf{V}^{+}(d^{3}X^{'}, d^{3}P^{'}, dV_{*}^{'}) d^{3}P_{*}^{'} \Delta t^{'} \ . \tag{9}$$

Modeling the collisional term by

$$C(E) \equiv \frac{\Delta N^{+} - \Delta N^{-}}{\Delta t} \, , \tag{10}$$

we finally arrive at the standard collisional Boltzmann equation

$$L(f) = \frac{\partial f}{\partial t} - Hp \frac{\partial f}{\partial p} = \\ = \int \int \left(f_{*}^{'} f^{'} - f_{*} f \right) \frac{\sqrt{g}}{E} d^{3}P_{*}\, \mathbf{V}(d^{3}X, d^{3}P, dV_{*}) = \\ \equiv C(E) \ .$$

Kinetic Entropy

The Entropy in the framework of kinetic theory is defined from the quantity

$$\Rightarrow \ s = - \int (f \ln f - f) p^{0} \frac{d^{3}p}{p^{0}} \ . \tag{11}$$

The equilibrium distribution function is the one that respects the property

$$f_{*(0)}^{'} f_{(0)}^{'} = f_{*(0)} f_{(0)} \, . \tag{12}$$

Taking the logarithm of the previous relation,

$$\ln f_{*(0)}^{'} + \ln f_{(0)}^{'} = \ln f_{*(0)} + \ln f_{(0)} \, . \tag{13}$$

The term lnf(0) is characterized as a sum-invariant and can therefore be expressed in the form [3].

$$\ln f(0) = a - b_{\mu} p_{\mu} \Rightarrow f(0) = a e^{-b_{\mu} p_{\mu}} \tag{14}$$

so that, generally speaking, we will assume from now on f(0) in the form

$$f_{(0)} \equiv e^{\alpha(t) - \beta(t) E} \, . \tag{15}$$

The (Classical) Boltzmann H Theorem

From there, the steps follow

• Define the quantity

$$H(t) \equiv \int f_{*} \ln f_{*} d^{3}p_{*} \ . \tag{16}$$

The quantity H, often called Boltzmann Entropy, was defined by Boltzmann in Lectures on Gas Theory (1896), and it is the first known concept related to entropy in the statistical approach.

• Calculate ∂H/∂t

$$\frac{\partial H}{\partial t} = \int (1 + \ln f_{*}) \left(f_{*}^{'} f^{'} - f_{*} f \right) d\sigma(t) d^{3}p d^{3}p_{*} = \\ = \frac{1}{2} \int \left[2 + \ln (f_{*} f) \right] \left(f^{'} f_{*}^{'} - f f_{*} \right) d\sigma(t) d^{3}p d^{3}p_{*} \ .$$

Exchanging the collisional role of the two qualities of particles and considering that classically

$$(d^3p' d^3p'_* = d^3p d^3p_*)$$

$$\frac{\partial H}{\partial t} = \frac{1}{2}\int \left[-2 - \ln\left(f'_* f'\right)\right]\left(f' f'_* - f f_*\right) d\sigma(t) d^3p d^3p_* \,. \tag{17}$$

• Summing the two last

$$\frac{\partial H}{\partial t} = \frac{1}{2}\int \ln\left(\frac{f_* f}{f'_* f'}\right)\left(f' f'_* - f f_*\right) d\sigma(t) d^3p d^3p_* \,. \tag{18}$$

Notice that both if $(f' f'_* > f f_*)$ than $(f' f'_* < f f_*)$

$$\frac{\partial H}{\partial t} \leq 0, \quad \forall t\,, \tag{19}$$

being identically zero when $(f' f'_* = f f_*)$.

The deduction of the so-called Boltzmann H Theorem is therefore presented, which comes from the kinetic definition of entropy (in empty space: n ≡ 0)

$$s = -k_B H$$

establishes the entropy increase principle of thermodynamics.

Kinetic Euler Relation

Substituting f(0) in s,

$$s = -n_{(0)}\alpha + \frac{\rho_{(0)}}{T} + \int f_{(0)} d^3p + O(\phi^2)\,. \tag{20}$$

Let us think, alternatively, about the integral that defines isotropic pressure in thermodynamic equilibrium

$$P_{(0)} \equiv \frac{1}{3}\int e^{(\alpha-\beta E)}\frac{p^2}{E} d^3p\,. \tag{21}$$

As

$$e^{(-\beta E)} = -\frac{1}{\beta}\frac{E}{p}\frac{d}{dp}e^{(-\beta E)} \tag{22}$$

in which $E = p^2/2$ was used, we arrive at

$$P = \frac{1}{3}\int e^{\alpha}\left[-\frac{1}{\beta}\frac{E}{p}\frac{d}{dp}e^{(-\beta E)}\right]\frac{p^2}{E} d^3p = \\ = -\frac{1}{3}\frac{4\pi}{\beta}\int p^3 \frac{d}{dp}\left[e^{(\alpha-\beta E)}\right] dp\,.$$

Integrating "by parts" (boundary terms omitted)

$$u = p^3 \rightarrow du = 3p^2 dp \tag{23}$$
$$dv = d\left[e^{(\alpha-\beta E)}\right] \quad \rightarrow \quad v = e^{(\alpha-\beta E)}\,.$$

$$P = -\frac{4\pi}{\beta}\left[-\int p^2 e^{(\alpha-\beta E)} dp\right] = \frac{1}{\beta}\int f_{(0)} d^3p\,.$$

Therefore

$$n = \int f_{(0)} d^3p = P\beta = \frac{P}{T} \quad \Rightarrow P = nT \tag{24}$$

Taking this result into (20), we conclude that

$$s = \frac{\rho_{(0)} + P_{(0)} - n_{(0)}\mu}{T} + O(\phi^2) \tag{25}$$

where (μ ≡ αT).

This result corresponds to the Euler relation obtained via kinetic formulation.

Final Considerations

In the present text, starting from the thermodynamic definition of entropy formulated by Clausius, we establish the conditions of reversibility of thermodynamic systems (Clausius Theorem).

Clausius' definition of entropy allowed us to conclude that the principle of increasing entropy in thermodynamic systems remains valid.

Having done this, we move on to dealing with entropy from a statistical point of view. Firstly, we discuss Boltzmann's intuition about what form entropy should have in statistical formulation. From the analysis carried out on a system initially composed of two thermally isolated reservoirs that, from a given moment, begin to interact (exchange heat), we arrived at a statistical form corresponding to the thermodynamic definition for temperature.

In other words, we determine the relationship between the thermodynamic (temperature) and statistical concepts for entropy.

Next, starting from the definitions of equilibrium distribution function and Boltzmann's (standard collisional) equation, we recover, from Boltzmann's H theorem, the validity of the principle of entropy growth.

Finally, in Appendix, we discuss how entropic evolution occurs in an ideal gas performing the Carnot Cycle. From there we conclude that, as stated in Clausius' theorem, reversible thermodynamic systems have zero entropy variation.

Appendix A: Classical Thermodynamics

Entropy of an Ideal Gas in the Carnot Cycle

In a Carnot Cycle (reversible) the following property holds: the ratio between the heat exchanged Q1 (Hot) and Q2 (Cold) with the sources during a cycle is equal to the ratio between the temperatures T1 and T2 from sources, that is:

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \;\Rightarrow\; \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \equiv \Delta S = 0\,. \qquad \text{(A1)}$$

For a perfect gas undergoing isothermal expansion, there is no change in the internal energy (ΔU = 0) of the gas: the amount of heat received is completely

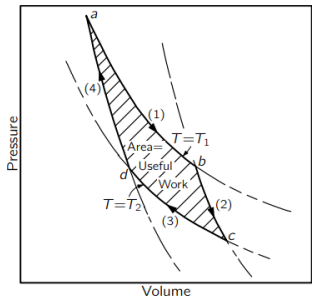

Figure 2: No Heat Engine that Operates Between a Given Hot Source and a Given Cold Source Can Have a Higher Efficiency than a Carnot Engine; and All Carnot Engines that Operate Between two Sources will have the Same Efficiency

converted into work

$$W = \int_{\mathrm{a}}^{\mathrm{b}} P dV \equiv Q_1\,.$$

During the expansion

$$PV = nRT \;\Rightarrow\; Q_1 = \int_{\mathrm{a}}^{\mathrm{b}} nRT_1 \frac{dV}{V} = nRT_1 \ln\left(\frac{V_{\mathrm{b}}}{V_{\mathrm{a}}}\right)$$

$$\therefore\; \boxed{\frac{Q_1}{T_1} = nR \ln\left(\frac{V_{\mathrm{b}}}{V_{\mathrm{a}}}\right)}\,.$$

Q_1 is, therefore, the heat received from the reservoir at

In isothermal compression from c to d, the heat delivered to the reservoir at T_2 by the system is

$$\boxed{Q_2 = nRT_2 \ln\left(\frac{V_c}{V_d}\right)}$$

To finish this analysis, we need to find the values for the relations (V_b/V_a) and (V_c/V_d).

To do so, consider an adiabatic expansion from b to c. Assuming the adiabatic condition, (PV) is constant.

$$\Rightarrow PV = nRT \quad \text{so} \quad \boxed{\frac{T_1}{V_b} = \frac{T_2}{V_c}} \qquad (A2)$$

Finally, the last process to close the thermodynamic cycle (adiabatic contraction) establishes

$$\Rightarrow \boxed{\frac{T_1}{V_a} = \frac{T_2}{V_d}} \qquad (A3)$$

Dividing (A3) by (A2)

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} \Rightarrow \frac{Q_1}{T_1} = nR\ln\left(\frac{V_b}{V_a}\right) = \frac{Q_2}{T_2}$$

Therefore

$$\boxed{\frac{Q_1}{T_1} = \frac{Q_2}{T_2}}$$

The last relation suggests that if we call (Q/T) something, we can say:
"In a Reversible process, the same amount of (Q/T) absorbed is released: there is no gain or loss of (Q/T)". This quantity is called Entropy (S).

Entropy in Reversible Paths

Suppose, for some hypothetical substance, the expansion of the thermodynamic state a (P_a,V_a,T_a) to b (P_b,V_b,T_b) (Figure.1).

Consider, furthermore, that associated with each step i (in V) in the expansion there is a thermal reservoir at the same temperature $T_{(i)}$ as the substance along the way. We can establish the condition that, at each step in V , an amount $dQ_{(i)}$ of heat is removed from the system and deposited in its respective thermal reservoir.

From here, connect all these thermal reservoirs through reversible heat machines that , from the $dQ_{(i)}$ received, perform $dW_{(i)}$ and establish contact of the system with a conventional cold source at the temperature of 1◦:

T_{cold} = T2 ≡ 1◦.

So that the total entropy required to go from a to b can be estimated as

$$\Rightarrow \Delta S = \sum_i \frac{dQ_{(i)}}{T_{(i)}} = \int_a^b \frac{dQ}{T} \ .$$

Appendix B: Macroscopic Euler's Relation

It is known from the fundamental postulates of thermodynamics that

$$U = U(S,V,N) \qquad (B1)$$

in which, considering first order homogeneity in U

$$\Rightarrow U(\lambda S,\lambda V,\lambda N) = \lambda U(S,V,N) \ . \qquad (B2)$$

Deriving the previous one with respect to λ

$$\frac{\partial U(\lambda S,...)}{\partial(\lambda S)}\frac{\partial(\lambda S)}{\partial\lambda}+\frac{\partial U(...,\lambda V,...)}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial\lambda}+$$

$$+\frac{\partial U(...,\lambda N)}{\partial(\lambda N)}\frac{\partial(\lambda N)}{\partial\lambda}=U(S,V,N)\,. \qquad \text{(B3)}$$

Using the thermodynamic definitions for (ρ, P, μ, T) with (s ≡ S/V).

$$dU = TdS - PdV + \mu dN\,, \quad \text{(B4)}$$

isolating (S) and dividing the resulting equation by (V) we arrive macroscopically at Euler Relation

$$\boxed{s=\frac{\rho+P-\mu n}{T}} \qquad \text{(B5)}$$

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