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# Thermodynamic Hamiltonian and Entropy Production

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## Abstract

The variational method holds considerable significance within mathematical and theoretical physics. Its importance stems from its capacity to characterise natural systems through physical quantities, irrespective of the chosen frame of reference. This characteristic makes it a powerful tool for understanding the behaviour of diverse physical phenomena. A global and statistical approach originating from the principles of non-equilibrium thermodynamics has been developed. This approach culminates in the principle of maximum entropy generation, specifically tailored for open systems. The principle itself arises as a direct consequence of applying the Lagrangian approach to open systems. The work focuses on a generalised method for deriving the thermodynamic Hamiltonian. This Hamiltonian is essential to the dynamical analysis of open systems, allowing for a detailed examination of their time evolution. The analysis suggests that irreversibility appears to be a fundamental process related to the evolution of states within open systems.

**Keywords:** dynamical systems; entropy; non-equilibrium thermodynamics; rational thermodynamics; irreversibility

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## 1. Introduction

The variational method holds significant importance in mathematical and theoretical physics, serving as a cornerstone for describing natural systems through frame-independent physical quantities [1]. This approach, particularly through the Lagrangian formulation, reveals underlying structural analogies across a diverse range of physical phenomena. A key outcome of employing the variational principle is the development of both global and local theories. Global theories offer insights into the average behaviour of physical quantities, while local theories delve into their specific distributions [2,3].

Furthermore, the concepts of entropy and its production, central to modern thermodynamics and statistical physics, are crucial to understanding equilibrium and non-equilibrium processes [4–7]. Entropy quantifies the progression of dissipative processes, with foundational contributions by Clausius and Prigogine. The application of a Lagrangian framework to entropy production, also termed entropy generation or irreversible entropy, has provided valuable mathematical insights into its behaviour [6].

Currently, research into non-equilibrium and far-from-equilibrium systems finds broad applicability across numerous fields, including biology, biotechnology, nanotechnology, ecology, climate change, energy optimisation, thermo-economics, phase separation, ageing processes, system theory and control, pattern formation, cancer pharmacology, DNA medicine, metabolic engineering, and chaotic/dynamical systems. These diverse areas often involve non-linear, dissipative, and open systems, highlighting the need for a unified analytical method like the variational principle [8].

However, existing variational principles often face limitations. It has been demonstrated that a useful variational principle cannot be derived without considering work, and entropy production for a system and its reservoir can only be obtained under specific conditions, such as a single heat bath at a constant temperature. Many current variational principles are confined to closed or isolated systems and have not been adequately linked to these fundamental requirements for open systems. In engineering thermodynamics and thermal physics, while open systems are analysed using entropy generation, the absence of a statistical definition hinders its extension to disciplines requiring a statistical approach. Conversely, statistical models, while powerful, often lack the generality for a universal approach, thus not serving as a general principle of investigation.

It is thought that thermodynamic laws are linked to random processes occurring within a system, which is why deterministic mechanical systems cannot be accurately described using a thermodynamic perspective. In Ref. [9], it was demonstrated that a thermodynamic framework can be established even for deterministic Hamiltonian systems. The study reveals that for Hamiltonian systems, it is feasible to define the concepts of a thermodynamic state, a thermodynamic process, and thermodynamic cycles. Additionally, in Ref. [10], a thermodynamic framework using symplectic geometry was obtained, allowing for the characterisation of all thermodynamic processes within the context of Analytic Mechanics. The primary outcome was the establishment of an extended phase space in which the equations of state for thermodynamics are manifested as constraints. This formalism was applied in representative cases focusing on van der Waals and Clausius gases. From the literature [11], we can highlight that the thermodynamic Lagrangian approach can be used when conditions are close to local thermodynamic equilibrium, as it does not account for non-linear and inertial effects adequately. Lagrangian techniques can be used to model phenomena in non-equilibrium states, like turbulent flows, and to analyse the thermodynamic costs and optimal driving conditions of systems far from steady states. However, its limitation lies in its use for local thermodynamic equilibrium in real systems.

This paper proposes the Gouy–Stodola theorem as a unifying general variational principle. It demonstrates the theorem's adherence to the aforementioned requirements and establishes its connection to statistical results concerning entropy production and generation. Additionally, an algebraic–geometric approach is presented for analysing irreversible thermodynamic systems and applying entropy generation within a dynamical system framework. Theoretical and mathematical physics frequently engage with idealised systems, and a persistent challenge lies in understanding the relationship between these idealisations and real-world systems.

This paper aims to establish a general, rational thermodynamic approach for analysing irreversible systems and to explore the application of entropy generation from a dynamical perspective. To achieve this, Section 2 will introduce the thermodynamic open system (the real system), Section 3 will detail the relationship between the thermodynamic Lagrangian and entropy generation, and Section 4 will cover the thermodynamic Hamiltonian and its application to thermodynamics.

## 2. Materials and Methods

### *2.1. The System Considered*

This section will delineate the system under consideration. To achieve this, the definition of a 'system with perfect accessibility' will be established. This definition will then serve as a foundation for characterising both the thermodynamic and dynamical systems relevant to the discussion. The concept of a 'system with perfect accessibility' is crucial. This implies that all parts of the system are equally and instantaneously accessible for observation or manipulation. This allows for a simplified model where the system's behaviour can be understood without the complexities of limited access or interaction. The first category encompasses open continuum systems. These systems are characterised by a continuous distribution of matter and energy, and they are open, meaning that they can exchange matter and energy with their surroundings. Examples of these systems could include fluid dynamic models or the behaviour of a gas within a defined space. The second category involves discrete $N-$particle systems. These systems consist of a finite number, $N$, of individual particles. These particles could be atoms, molecules, or any other distinct entity. The behaviour of these particles and their interactions form the basis of the system's dynamics. The number of particles, $N$, is a key parameter in defining the system's complexity and behaviour.

The subject under consideration pertains to the spatial configuration of a system's constituent elements. Specifically, each element, indexed by the subscript $i$, is definitively positioned within the system's framework. This positioning is achieved through the utilisation of a position vector $\mathbf{x}_i \in \mathbb{R}^3$, which has a velocity $\dot{\mathbf{x}}_i \in \mathbb{R}^3$, a mass $m_i \in \mathbb{R}$, and a momentum $\mathbf{p} = m_i \dot{\mathbf{x}}_i$, with $i \in [1, N]$ and $\mathbf{p} \in \mathbb{R}^3$ [8]. The masses $m_i$ must satisfy the condition

$$\sum_{i=1}^{N} m_i = m \tag{1}$$

where $m$ is the total mass. The total mass must be a conserved quantity, so that it follows that

$$\dot{\rho} + \rho \nabla \cdot \dot{\mathbf{x}}_B = 0 \tag{2}$$

where $\rho = dm/dV$ is the total mass density, with $V$ total volume of the system, and $\dot{\mathbf{x}}_B \in \mathbb{R}^3$, defined as $\dot{\mathbf{x}}_B = \sum_{i=1}^{N} \mathbf{p}_i / m$, is the velocity of the centre of mass. The mass density must satisfy the following conservation law [8]:

$$\dot{\rho}_i + \rho_i \nabla \cdot \dot{\mathbf{x}}_i = \rho \Xi \tag{3}$$

where $\rho_i$ is the density of the $i-$th elementary volume $V_i$, with $\sum_{i=1}^{N} V_i = V$, and $\Xi$ is the source, generated by matter transfer, chemical reactions, and thermodynamic transformations. This open system can be mathematically defined as follows [8].

**Definition 1** ([12]). *A dynamical state of N particles can be specified by the* $3N$ *canonical coordinates* $\left\{ \mathbf{q}_i \in \mathbb{R}^3, i \in [1, N] \right\}$ *and their conjugate momenta* $\left\{ \mathbf{p}_i \in \mathbb{R}^3, i \in [1, N] \right\}$. *The* $6N-$*dimensional space spanned by* $\left\{ (\mathbf{p}_i, \mathbf{q}_i), i \in [1, N] \right\}$ *is called the phase space* $\Omega$. *A point* $\sigma_i = (\mathbf{p}_i, \mathbf{q}_i)_{i \in [1,N]}$ *in the phase space* $\Omega := \left\{ \sigma_i \in \mathbb{R}^{6N} : \sigma_i = (\mathbf{p}_i, \mathbf{q}_i), i \in [1, N] \right\}$ *represents a state of the entire* $N-$*particle system.*

**Definition 2** ([8]). *A system with perfect accessibility* $\Omega_{PA}$ *is a pair* $(\Omega, \Pi)$, *with* $\Pi$ *being a set whose elements* $\pi$ *are called process generators, together with two functions:*

$$\pi \mapsto \mathcal{S} \tag{4}$$

$$\left(\pi^{'},\pi^{''}\right)\mapsto\pi^{''}\pi^{'} \tag{5}$$

*where $\mathcal{S}$ is the state transformation induced by $\pi$, whose domain $\mathcal{D}(\pi)$ and range $\mathcal{R}(\pi)$ are non-empty subsets of $\Omega$. This assignment of transformation to process generators is required to satisfy the following conditions of accessibility:*

1. $\Pi\sigma := \{\mathcal{S}\sigma : \pi\in\Pi, \sigma\in\mathcal{D}(\pi)\} = \Omega$, $\forall\sigma\in\Omega$: *The set $\Pi\sigma$ is called the set of the states accessible from $\sigma$, and consequently, it is the entire* state space, *the phase space $\Omega$;*
2. *If $\mathcal{D}(\pi'')\cap\mathcal{R}(\pi')\neq 0 \Rightarrow \mathcal{D}(\pi''\pi') = \mathcal{S}_{\pi'}^{-1}(\mathcal{D}(\pi''))$ and $\mathcal{S}_{\pi''\pi'}\sigma = \mathcal{S}_{\pi''}\mathcal{S}_{\pi'}\sigma\ \forall\sigma\in\mathcal{D}(\pi''\pi')$.*

**Definition 3** ([8])**.** *A process in $\Omega_{PA}$ is a pair $(\pi,\sigma)$, with $\sigma$ being a state and $\pi$ being a process generator such that $\sigma$ is in $\mathcal{D}(\pi)$. The set of all processes of $\Omega_{PA}$ is denoted by*

$$\Pi\diamond\Omega = \{(\pi,\sigma) : \pi\in\Pi, \sigma\in\mathcal{D}(\pi)\} \tag{6}$$

*If $(\pi,\sigma)$ is a process, then $\sigma$ is called the initial state for $(\pi,\sigma)$, and $\mathcal{S}\sigma$ is called the final state for $(\pi,\sigma)$.*

**Definition 4** ([3])**.** *A thermodynamic system is a system with perfect accessibility $\Omega_{PA}$ with two actions $W(\pi,\sigma)\in\mathbb{R}$ and $H(\pi,\sigma)\in\mathbb{R}$, called work performed and heat gained by the system during the process $(\pi,\sigma)$, respectively.*

**Definition 5** ([8])**.** *A thermodynamic path $\gamma$ is an oriented piecewise continuously differentiable curve in $\Omega_{PA}$.*

**Definition 6** ([8])**.** *A cycle $\mathcal{C}$ is a path whose endpoints coincide.*

**Definition 7** ([13])**.** *A family $\mathcal{F}$ of subset of a perfect accessibility phase space $\Omega_{PA}$ is said to be an* algebra *if the following conditions are satisfied:*

1. $\Omega_{PA}\in\mathcal{F}$;
2. $\Omega_{PA}^{0}\in\mathcal{F}\Rightarrow\Omega_{PA}^{0^c}\in\mathcal{F}$;
3. $\{\Omega_{PA_i}\}_{i\in[1,k]}\subset\mathcal{F}\Rightarrow\bigcup_{i=1}^{k}\Omega_{PA_i}\in\mathcal{F}$.

**Comment 1** ([8])**.** *The set of all these stationary states of a system $\Omega_{PA}$ is called a non-equilibrium ensemble.*

**Comment 2** ([8])**.** *Concerning the definition of an algebra, we can highlight that*

1. $\emptyset\in\mathcal{F}$;
2. *The algebra $\mathcal{F}$ is closed under countable intersections and subtraction of sets;*
3. *If $k\equiv\{\infty\}$ then $\mathcal{F}$ is said to be a $\sigma-$algebra.*

**Definition 8** ([13])**.** *A function $\mu:\mathcal{F}\to[0,\infty)$ is a measure if it is additive. This means that for any countable subfamily $\{\Omega_i, i\in[1,n]\}\subseteq\mathcal{F}$ consisting of mutually disjoint sets, it follows that*

$$\mu\left(\bigcup_{i=1}^{n}\Omega_i\right)=\sum_{i=1}^{n}\mu(\Omega_i) \tag{7}$$

*It also follows that*

1. $\mu(\emptyset)=0$;
2. *If $\Omega_\alpha,\Omega_\beta\in\mathcal{F}$ and $\Omega_\alpha\subset\Omega_\beta\Rightarrow\mu(\Omega_\alpha)\leq\mu(\Omega_\beta)$;*
3. *If $\Omega_1\subset\Omega_2\subset\cdots\subset\Omega_n$ and $\{\Omega_i, i\in[1,n]\}\in\mathcal{F}\Rightarrow\mu(\bigcup_{i=1}^{n}\Omega_i)=\sup_i\mu(\Omega_i)$.*

*Moreover, if $\mathcal{F}$ is a $\sigma-$algebra and $n \equiv \{\infty\}$, then the measure is said to be $\sigma-$additive.*

**Definition 9** ([14])**.** *A smooth map $\mathcal{S}$ of a compact manifold $\mathcal{M}$ is a map with the property that around each point $\sigma$, we can established a system of coordinates based on smooth surfaces $W^s_\sigma$ and $W^u_\sigma$, with s = stable and u = unstable, of complementary positive dimension which has the following characteristics:*

1. Covariant: $\partial\mathcal{S}W^i_\sigma = W^i_{\mathcal{S}\sigma}, i = u, s$. *This means that the tangent planes $\partial\mathcal{S}W^i_\sigma, i = u, s$ to the coordinate surface at $\sigma$ are mapped over the corresponding planes at $\mathcal{S}\sigma$;*
2. Continuous: $\partial\mathcal{S}W^i_\sigma$, *with $i = u, s$, depends continuously on $\sigma$;*
3. Transitivity: *There is a point in a subsystem of $\Omega_{PA}$ of zero Liouville probability, called an attractor, with a dense orbit.*

**Comment 3** ([8])**.** *A significant number of systems also meet the* hyperbolic condition: *when a tangent vector $\mathbf{v}$ is acted upon by $\mathcal{S}^{-k}$, its length is increased by a factor of $C\lambda^k$ for $k > 0$, where $C > 0$ and $\lambda < 1$. This implies that if an observer travels with point $\sigma$, they will perceive the nearby points moving around it as though it were a hyperbolic fixed point. However, from a broader perspective, it is not essential to introduce this condition.*

**Hypothesis 1** ([8])**.** *There exists a statistics $\mu_{PA}$ describing the asymptotic behaviour of almost all initial data in perfect accessibility phase space $\Omega_{PA}$ such that except for a volume zero set of initial data $\sigma$,*

$$\lim_{T \longrightarrow \infty} \frac{1}{T} \sum_{j=1}^{T-1} \varphi\left(\mathcal{S}^j \sigma\right) = \int_\Omega \mu_{PA}(d\sigma)\varphi(\sigma) \tag{8}$$

*for all continuous functions $\varphi$ on $\Omega_{PA}$ and for every transformation $\sigma \mapsto \mathcal{S}_t(\sigma)$. For hyperbolic systems the distribution $\mu_{PA}$ is the Sinai–Ruelle–Bowen distribution (SRB-distribution or SRB-statistics)* [15].

**Comment 4** ([8])**.** *The notation $\mu_{PA}(d\sigma)$ hints at a potential fractal character of the support of the distribution $\mu$. This suggests that the likelihood of locating the dynamical system within the infinitesimal volume $d\sigma$ surrounding $\sigma$ might not be directly proportional to $d\sigma$. As a result, it cannot simply be expressed as $\mu_{PA}(\sigma)d\sigma$; instead, it must be conventionally written as $\mu_{PA}(d\sigma)$. The concept of fractal phase space is still a topic of active discussion* [16]*, yet there is substantial evidence for it in low-dimensional systems (refer to* [16,17]*). In this context, we aim to explore this possibility further.*

**Definition 10** ([8])**.** *The triple $(\Omega_{PA}, \mathcal{F}, \mu_{PA})$ is a* measure space*, the* Kolmogorov probability space $\Gamma$.

**Definition 11** ([8])**.** *A dynamical law $\tau$ is a group of measure-preserving automorphisms $\mathcal{S} : \Omega_{PA} \rightarrow \Omega_{PA}$ of the probability space $\Gamma$.*

**Definition 12** ([7])**.** *A dynamical system $\Gamma_d = (\Omega_{PA}, \mathcal{F}, \mu_{PA}, \tau)$ consists of a dynamical law $\tau$ on the probability space $\Gamma$.*

### 2.2. Thermodynamic Lagrangian and Entropy Generation

The fields of theoretical and mathematical physics focus on idealised systems, and a key challenge lies in understanding how these idealisations relate to real-world phenomena. In exploring irreversibility, the concept of thermostats has been introduced. These are systems of particles that move outside the main system and interact with its particles through the walls of the system itself. In the statistical and dynamical study of thermodynamics, Gallavotti identifies the essential quantity of entropy production, denoted by $\sigma_{entr}$, which is defined as follows [14]:

$$\sigma_{entr} = k_B \sigma_{+}^{entr} = -k_B \int_{\Omega} \mu_{PA}(d\sigma) \nabla \cdot \mathbf{E}(\sigma) \tag{9}$$

with always $\sigma_{+}^{entr} \geq 0$ and $\sigma_{+}^{entr} = 0$ only for the equilibrium state and $\mathbf{E}(\sigma) := \mathbf{f}_{int}(\sigma) + \mathbf{f}_{nc}(\sigma) + \mathbf{f}_{term}(\sigma)$, with $\mathbf{f}_{int}(\sigma)$ being the internal conservation force, $\mathbf{f}_{nc}(\sigma)$ being the external active non-conservative force, and $\mathbf{f}_{term}(\sigma)$ being the thermostatic expression.

**Comment 5** ([3])**.** *In accordance with Truesdell [2], for any continuum thermodynamic system—whether isolated, closed, or open—it is feasible to identify a thermodynamic subsystem characterized by an elementary mass* $dm$ *and an elementary volume* $dV = dm/\rho$, *where* $\rho$ *represents the mass density [2,3,8]. The thermodynamic framework can then be developed based on these generalised coordinates* $\{\xi_i, \dot{\xi}_i, t\}_{i \in [1,N]}$, *with* $\xi_i = \alpha_i - \alpha_i^{(0)}$, $\alpha_i$ *being the extensive thermodynamic quantities and* $\alpha_i^{(0)}$ *being their values in the stable states.*

In engineering thermodynamics, the energy lost for irreversible processes is evaluated by the first and second laws of thermodynamics for open systems; consequently, the following definition can be introduced.

**Definition 13** ([8])**.** *Entropy generation* $\Delta S_g$ *is defined as*

$$\frac{W_{lost}}{T_a} = \Delta S_g := \frac{Q_r}{T_a}\left(1 - \frac{T_a}{T_r}\right) + \frac{\Delta H}{T_a} - \Delta S + \frac{\Delta E_k + \Delta E_g - W}{T_a} \tag{10}$$

*where* $W_{lost}$ *is the work lost for irreversibility,* $T_a$ *is the temperature of the lower reservoir,* $Q_r$ *is the heat source,* $T_r$ *is its temperature,* $T_a$ *is the ambient temperature,* $H$ *is the enthalpy,* $S$ *is the entropy,* $E_k$ *is the kinetic energy,* $E_g$ *is the gravitational energy, and* $W$ *is the work.*

**Comment 6** ([8])**.** *It has been proved that* $\Delta S_g = \dot{m}\sigma_{entr}$, *with* $\dot{m}$ *mass flow.*

**Theorem 1** ([3])**.** *The thermodynamic Lagrangian can be obtained as*

$$\mathcal{L} = -T_a \Delta S_g \tag{11}$$

**Proof.** For every subsystem a thermodynamic Lagrangian $\rho_{\mathcal{L}}$ per unit time $t$, temperature $T$, and volume $V$ is defined as [3]

$$\rho_{\mathcal{L}} = \frac{d^3\mathcal{L}}{dVdTdt} = \frac{d\dot{S}}{dV} - \psi \tag{12}$$

where [3]

$$\frac{d\dot{S}}{dV} = \sum_{ij} L_{ij}\xi_i\xi_j + \frac{1}{2}\sum_{ijk} L_{ijk}\xi_i\xi_j\xi_k \tag{13}$$

is the entropy per unit time and volume and $\psi$ is the non-linear dissipative potential density, defined as [8]

$$\psi = \frac{1}{2}\sum_{ij} L_{ij}\xi_i\xi_j + \frac{1}{6}\sum_{ijk} L_{ijk}\xi_i\xi_j\xi_k \tag{14}$$

Above, $L_{ij}$ are the Onsager coefficients, defined as [18]

$$L_{ij} = \frac{1}{2}\int_{-\infty}^{\infty} \mu_{PA}\left[\sigma_i(\mathcal{S}_t\sigma)\sigma_j(\sigma)\right]_{\mathbf{E}=\mathbf{0}} dt \tag{15}$$

where $\sigma_\alpha$, with $\alpha = i, j$, is the $\alpha$-state and $\mathbf{E} = \{E_k\}_{k\in[1,r]}$ represents the $r$ external forces. Consequently, $\rho_{\mathcal{L}}$ becomes

$$\rho_{\mathcal{L}} = \frac{1}{2}\sum_{ij} L_{ij}\xi_i\xi_j + \frac{1}{3}\sum_{ijk} L_{ijk}\xi_i\xi_j\xi_k \tag{16}$$

which is also the Legendre transformation to relation (14) [3]. Moreover, the thermodynamic Lagrangian $\mathcal{L}$ is defined as

$$\mathcal{L} := \int_t dt \int_T dT \int_V dV \rho_{\mathcal{L}} \tag{17}$$

Consider that [3]

$$\rho_{\mathcal{L}} = \rho_S - \rho_\pi - \psi \tag{18}$$

where $\rho_S$ is the entropy per unit time and mass, and $\rho_\pi$ is the power per unit mass and temperature. Now, following Lavenda (Lucia 2008 [8]), $\rho_S - \rho_\pi = 2\psi$; therefore,

$$\rho_{\mathcal{L}} = \psi \tag{19}$$

and

$$\int_t dt \int_T dT \int_V dV \rho_{\mathcal{L}} = \int_t dt \int_T dT \int_V dV \psi \tag{20}$$

so it follows that

$$\mathcal{L} = \int_t dt \int_T dT \int_V dV \psi \tag{21}$$

But, remembering that

$$W_{lost} := \int_t dt \int_T dT \int_V dV \psi \tag{22}$$

we can obtain

$$\mathcal{L} = W_{lost} \tag{23}$$

Considering the Gouy–Stodola theorem [3], which states that

$$W_{lost} = -T_a \Delta S_g \tag{24}$$

Equation (11) becomes

$$\mathcal{L} = \int_t dt \int_T dT \int_V dV \psi = -T_a \Delta S_g \tag{25}$$

with $T_a$ being the temperature of the lower reservoir and $S_g$ being the entropy generation [3]. □

**Definition 14** ([8]). *The statistical expression for the irreversible-entropy variation is thus*

$$\Delta S_g = -\frac{k_B}{\dot{m}} \int_\Omega \mu_{PA}(d\sigma)\nabla \cdot \mathbf{E}(\sigma) \tag{26}$$

**Theorem 2** ([8]). *The principle of maximum entropy generation* [8]: *The condition of stability for the open system's stationary states is that its entropy generation* $\Delta S_g$ *reaches its maximum:*

$$\delta(\Delta S_g) \geq 0 \tag{27}$$

**Proof.** The thermodynamic action is defined as (Truesdell 1970 [2])

$$\mathcal{A} := \int_t dt \mathcal{L} \tag{28}$$

From the principle of the least action,

$$\delta\mathcal{A} \leq 0 \tag{29}$$

and remembering relation (11), it follows that

$$-\delta\left(\int dt T_a \Delta S_g\right) \leq 0 \tag{30}$$

which becomes

$$\delta\left(T_a \Delta S_g\right) \geq 0 \tag{31}$$

And, if $T_a$ is constant,

$$\delta\left(\Delta S_g\right) \geq 0 \tag{32}$$

□

## 3. Results

In this section, we introduce the thermodynamic Hamiltonian for open systems as a result of the analytical flow depicted in the previous section.

**Theorem 3.** *The thermodynamic Hamiltonian: The thermodynamic Hamiltonian can be obtained as* $T_a\Delta S_g$.

**Proof.** The thermodynamic Hamiltonian density $\rho_{\mathcal{H}}$ can be defined following the definition of the thermodynamic Lagrangian density $\rho_{\mathcal{L}}$:

$$\rho_{\mathcal{H}} = \sum_i \zeta_i \xi_i - \rho_{\mathcal{L}} \tag{33}$$

with

$$\zeta_i = \frac{\partial \rho_{\mathcal{L}}}{\partial \dot{\xi}_i} \tag{34}$$

being the conjugate generalised momentum to the generalised coordinates $\xi_i$. The thermodynamic Lagrangian density $\rho_{\mathcal{L}}$ is defined by relation (12), and it is a function only of the generalised coordinates, so that it follows that

$$\frac{\partial \rho_{\mathcal{L}}}{\partial \dot{\xi}_i} = 0 \tag{35}$$

Consequently, the thermodynamic Hamiltonian density is

$$\rho_{\mathcal{H}} = -\rho_{\mathcal{L}} \tag{36}$$

and the thermodynamic Hamiltonian can be obtained as

$$\begin{aligned}\mathcal{H} = \int_t dt \int_T dT \int_V dV \rho_{\mathcal{H}} = -\int_t dt \int_T dT \int_V dV \rho_{\mathcal{L}} = \\ = -\mathcal{L} = T_a \Delta S_g\end{aligned} \tag{37}$$

□

**Comment 7.** *From the definition of action, it follows that the thermodynamic action can be written as*

$$\mathcal{A} = \int_t dt\mathcal{L} = -\int_t dt\mathcal{H} \tag{38}$$

**Comment 8.** *The thermodynamic Hamiltonian for open systems is related only to entropy generation. Consequently, this quantity seems to be the basis of the analysis of these systems.*

**Comment 9.** *Moreover, the irreversibility seems to be the fundamental phenomenon which drives the evolution of the states of the open systems.*

**Comment 10.** *From relation* (35)*, it follows that*

$$\zeta_i = 0 \Leftrightarrow \dot{\zeta}_i = 0 \Leftrightarrow \frac{\partial \mathcal{H}}{\partial \xi_i} = 0 \Leftrightarrow \frac{\partial \rho_{\mathcal{H}}}{\partial \xi_i} = 0 \tag{39}$$

*and as a consequence of relation* (16)*, it is possible to obtain*

$$\psi = \rho_{\mathcal{L}} = -\rho_{\mathcal{H}} = \frac{1}{6} \sum_{ijk} L_{ijk} \xi_i \xi_j \xi_k \tag{40}$$

*proving the completely non-linear behaviour of irreversibility and dissipation.*

**Comment 11.** *From relation* (35)*, it follows that*

$$\dot{\xi}_i = \frac{\partial \rho_{\mathcal{H}}}{\partial \zeta_i} = 0 \tag{41}$$

*so*

$$\xi_i = constant \tag{42}$$

*proving that dissipation does not vary the velocity of the points inside the phase space, but it varies the path, in agreement with the hypothesis by Jaynes* [5].

## 4. Discussion

Over the past twenty years, classical thermodynamics has progressed from phenomenological approaches to a more sophisticated framework grounded in Hamiltonian theory [19]. This advancement has allowed the theories of thermal physics and engineering thermodynamics to be placed on par with analytical mechanics [20]. Notably, thermodynamic and mechanical systems can be integrated into a unified non-linear dynamical theory which describes both equilibrium and non-equilibrium processes [21]. This is accomplished by developing homogeneous Hamiltonian functions of the first degree in momenta within an extended thermodynamic phase space, using various representations. This area of research is significant, particularly considering the century-long evolution of Hamiltonian theory, which has led to the establishment of a modern geometric (differential) framework. Key theorems and methods that aid in identifying time-invariant structures in phase space or constants of motion have been discovered. Fields such as chemical [22] and statistical thermodynamics [23,23,24], as well as spectroscopy, have benefited from these approaches, particularly in understanding the properties of highly excited molecules. The identification of transition states in chemical reactions and solid-state processes as hyperbolic invariant manifolds within molecular phase space has enhanced our comprehension of these phenomena. The mathematical abstraction and generalisation of geometric Hamiltonian theory in phase space create a unified computational framework that bridges the microscopic and macroscopic realms [25–27]. In the area of multi-physics system modelling, a variant of Hamiltonian theory known as port-Hamiltonian systems theory has been developed, finding applications across mechanics, chemistry, electromagnetism, hydrodynamics [28] and fluid dynamics [29], and control disciplines [30,31]. Additionally, advancements in quantum thermodynamics have enabled the modelling of quantum mechanical systems interacting with thermal baths, in alignment with thermodynamic principles.

Now, we wish to show a possible application of the result obtained, i.e., the use of the entropy generation approach in an engineering context of Hamiltonian systems.

Transport phenomena, which involve the transfer of both mass and energy, play a fundamental role in systems that are not in equilibrium. This discussion will focus on mass transfer. Mass transfer can occur when a directional force is applied to the mass. Our approach is also useful for explaining the macroscopic effects of diffusion in a temperature gradient, specifically in relation to the Soret effect. This effect is significant in civil engineering, as it underlies the movement of water when a thermal bridge is present. When a specific portion of a bistable potential is heated, the relative stability of the two wells changes. As a result, some of the mass transfers from the heated well to the cooler one; this phenomenon is known as Landauer's blowtorch effect [32]. It is important to note that in Landauer's blowtorch effect, the temperature difference between two regions of a body causes mass transfer. Consequently, this temperature difference leads to the movement of mass. The origin of this phenomenon lies in the extra kinetic energy acquired by particles in the high-temperature region, which provides the energy necessary to overcome a potential barrier.

To analyse this phenomenon, we examine a system of $N$ Brownian particles, each with mass $m$, situated in a symmetric bistable potential $V(x)$, where $x$ denotes the position. This potential has a maximum at $x = 0$ and features two minima: one at $x = -x_{min}$ and the other at $x = x_{min}$. The system is maintained at a temperature $T$. We specifically heat the left segment of the potential, defined for $x \in [-x_1, -x_2]$, with temperatures $T_h$, ensuring that $-x_{min} \leq -x_1 \leq -x_2 \leq 0$. The peak at $x = 0$ serves as a potential barrier. Thus, the heat transfer from the high-temperature region to the lower-temperature region can be assessed as

$$Q = \int_{-x_1}^{-x_2} V(x)dx \tag{43}$$

Thus, the entropy variation is

$$S_g = \Delta S = \left(\frac{1}{T_h} - \frac{1}{T}\right)[V(-x_2) - V(-x_1)] \tag{44}$$

As a consequence, the density of the two relative populations in the steady state is modified as:

$$\frac{P_R}{P_L} = \frac{P_{R,eq}}{P_{L,eq}} exp\left\{\left(\frac{1}{T_h} - \frac{1}{T}\right)\left[V(-x_2) - V(-x_1)\right]\right\} \tag{45}$$

where $P$ is the integrated probability of residence of the particle in state $L$ or $R$; $L$ and $R$ mean left and right, respectively; and $eq$ means equilibrium. So, in this effect, the entropy increases as a consequence of flows of Brownian particles across a barrier, with a variation in the relative population density in the two wells [32]. Moreover, considering that

$$\frac{P_R}{P_L} - \frac{P_{R,eq}}{P_{L,eq}} = \frac{P_{R,eq}}{P_{L,eq}}\left(exp\left\{\left(\frac{1}{T_h} - \frac{1}{T}\right)\left[V(-x_2) - V(-x_1)\right]\right\} - 1\right) \tag{46}$$

the flow of mass is

$$\dot{m} = m\int_{-x_1}^{-x_2} n\frac{P_{R,eq}}{P_{L,eq}}\left(exp\left\{\left(\frac{1}{T_h} - \frac{1}{T}\right)\left[V(-x_2) - V(-x_1)\right]\right\} - 1\right)dx \tag{47}$$

where $n$ is the linear density of particles. Now, if $T_h - T << T$, then the mass flows becomes

$$\dot{m} = m\frac{P_{R,eq}}{P_{L,eq}}\left[\frac{T_h - T}{T^2}\Big(V(-x_2) - V(-x_1)\Big)\right]\int_{-x_1}^{-x_2} ndx \tag{48}$$

This application shows the utility of thermodynamics in diverse contexts. The microscopic effects provide a formal framework to describe the movement of masses resulting from energy (temperature) variations. This detailed perspective enables us to understand the broader effects employed in macroscopic physics, which forms the foundation of engineering. This example demonstrates how thermodynamics in bioengineering can offer a potent methodology for practical applications. The structured approach allows us to emphasise how integrating mathematical and physical principles can enhance this thermodynamic framework.

## 5. Conclusions

This study aims to establish a general rational thermodynamic approach for analysing irreversible systems. Our primary objective is to develop an application of entropy generation within these systems, utilising a dynamical approach. To achieve this, we systematically explore several key areas. Initially, in Section 2, we introduce the concept of the thermodynamic open system, representing a real-world system. Subsequently, in Section 3, we delve into the relationship between the thermodynamic Lagrangian and entropy generation. Following this, Section 4 focuses on the thermodynamic Hamiltonian and the Hamiltonian approach to thermodynamics.

The variational method holds significant importance in mathematical and theoretical physics. It enables us to describe natural systems using physical quantities, irrespective of the chosen frame of reference [1]. Furthermore, the Lagrangian formulation proves applicable across a diverse range of physical phenomena, highlighting structural analogies between different physical events [2]. The variational principle yields both local and global theories. The global theory provides direct insights into the mean values of physical quantities, while the local theory offers information about their distribution [2,3,8].

In non-equilibrium phenomena, irreversibility manifests through fluctuations in physical quantities. These fluctuations, which seemingly disrupt stationarity, occur symmetrically around their average values [18]. The concepts of entropy and its production in both equilibrium and non-equilibrium processes form the foundation of modern thermodynamics and statistical physics [4–7].

Entropy has been demonstrated to be a crucial quantity in describing the progression of non-equilibrium dissipative processes. Clausius, in the period of 1854–1862, made a significant contribution by introducing the concept of entropy in physics. Prigogine, in 1947, further advanced the field by proving the minimum entropy production principle [6]. A Lagrangian approach to this subject has allowed us to derive the mathematical implications for the behaviour of entropy generation, also known as entropy variation due to irreversibility, or irreversible entropy, denoted by $S_g$ [8].

The $\varepsilon$-steady state definition allows us to determine that for certain fluctuations, the probability of occurrence follows a universal law and the frequency of occurrence is governed by a quantity related to entropy generation. This quantity possesses a purely mechanical interpretation, linked to the ergodic hypothesis, which posits that an isolated system evolves, visiting all possible microscopic states. Moreover, considering the open system to be a system with perfect accessibility, represented as a probability space where a $PA$-measure is defined, a statistical approach has been developed [8].

Through this research study, we aim to provide a robust framework for understanding and analysing irreversible systems, contributing to the advancement of thermodynamic theory and its practical applications [5,33].

In conclusion, the Lagrangian thermodynamic framework presented here seeks to offer an understanding of both equilibrium and non-equilibrium systems. It emphasises that non-linear and inertial effects can be essential to characterising the macroscopic behaviour of systems that are far from equilibrium, although these effects allow its use only for systems in local thermodynamic equilibrium.

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