

Liouville’s Theorem as a Subtle Statement of the First Law of Thermodynamics

G. G. Nyambuya

National University of Science and Technology, Faculty of Applied Sciences – Department of Applied Physics,
Fundamental Theoretical and Astrophysics Group, P. O. Box 939, Ascot, Bulawayo, Republic of Zimbabwe.
E-mail: physicist.ggn@gmail.com

Just like the rest of the Laws of Thermodynamics, the First Law of Thermodynamics (FLT) is an empirical law firmly anchored on the unshakeable fertile soils of verifiable experimental philosophy. Be that as it may, this law (FLT) does not have a fundamental theoretical basis on which it is founded or rests upon. In the present paper, we demonstrate that Liouville’s Theorem (in physics) can be cast or can be seen as an expression of the FLT. In this way, one can thus envisage Liouville’s Theorem as a fundamental theoretical basis for the FLT.

A theory is the more impressive the greater the simplicity of its premises [are], the more different kinds of things it relates, and the more extended is its area of applicability ... Classical Thermodynamics ... is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown ... Albert Einstein (1879-1955). Adapted from [1, p. 227].

1 Introduction

The *First Law of Thermodynamics* (FLT) is a version of the *General Empirical Law of Conservation of Energy* (GELCE) applicable to thermodynamic systems. The GELCE states that the total energy of an isolated system is a constant of time; energy can only be transformed from one form to another, but can never be created nor destroyed. The FLT is often stated as follows:

$$dQ = dU + dW, \tag{1}$$

where dQ , dU and dW are the change in the heat content of a thermodynamic system that accompanies a change in the internal energy dU of the system, for an amount of work dW performed on the system. Simple stated: the heat content of a thermodynamic system dQ , equals the change in the internal energy dU , plus the amount of work dW done by the system on its surroundings. The FLT is an empirical law founded and strongly anchored on the fertile soils of experimental philosophy. There is no theoretical furnishment of this law. This paper makes an endeavour to proffer a theoretical justification of this law on the basis of Liouville’s theorem [2], i.e. we demonstrate that Liouville’s theorem can be viewed or can be seen as a statement of the FLT.

2 Liouville’s theorem

In physics, Liouville’s theorem [2], named after the great French mathematician Joseph Liouville (1809-1882), is a key

theorem in classical statistical thermodynamics and in Hamiltonian mechanics*. The theorem asserts that the probability density function ϱ , is a time-constant along the trajectories describing the system – in other words, the *density of states* in an ensemble of many identical states with different initial conditions is constant along every trajectory in phase space. This time-independent density of states is in statistical mechanics known as the classical “*a priori probability*” where an “*a priori probability*” is a probability that is derived purely from deductive reasoning.

The probability density function (or phase space distribution function) ϱ is assumed to depend on position ($\vec{r} = \vec{r}(t)$) and momentum ($\vec{p} = \vec{p}(t)$), i.e. $\varrho = \varrho(\vec{r}, \vec{p})$, and this probability density function is constant along the trajectories of the system – i.e. the density of states of the *system points* in the vicinity of a given system point traversing through phase space remains constant through the passage of time. Liouville’s theorem succinctly summarizes this through the equation:

$$\frac{d\varrho}{dt} = \frac{\partial\varrho}{\partial t} + \sum_{j=1}^N \dot{\vec{r}}_j \cdot \frac{\partial\varrho}{\partial \vec{r}_j} + \sum_{j=1}^N \dot{\vec{p}}_j \cdot \frac{\partial\varrho}{\partial \vec{p}_j} = 0. \tag{2}$$

Writing $\dot{\vec{r}}_j = \vec{v}_j$ and $\dot{\vec{p}}_j = \vec{F}_j$, the above can be written as:

$$\underbrace{-\frac{\partial\varrho}{\partial t}}_{\text{Term (I)}} = \underbrace{\sum_{j=1}^N \vec{v}_j \cdot \frac{\partial\varrho}{\partial \vec{r}_j}}_{\text{Term (II)}} + \underbrace{\sum_{j=1}^N \vec{F}_j \cdot \frac{\partial\varrho}{\partial \vec{p}_j}}_{\text{Term (III)}}, \tag{3}$$

where \vec{v}_j and \vec{F}_j , are the velocity and resultant force acting on the j^{th} particle respectively. The task of the present paper is to identify Terms (I), (II) and (III) of (3) with dQ , dU and dW , appearing in (1), respectively. In order for us to achieve this, it will require us to justly define – in an explicit manner – the

*There is also in complex analysis, Liouville’s theorem, named after the same Joseph Liouville, and this theorem states that every bounded *entire function* (i.e., *integral function*) must be constant.

probability density function ϱ , thereby resulting in Liouville's theorem being nothing more (albeit – very insightful) than a statement of the FLT. Before we can do this, we need to set up in the next section, a theory that can explain or describe the evolution of thermodynamic fluctuations.

3 Theory of thermodynamic fluctuations

In our theory of thermodynamic fluctuations, we begin in Section 3.1 by defining what these fluctuations really are and having done that, we proceed in Section 3.2 to define the phase space on which the evolution of these thermodynamic fluctuations is defined.

3.1 Definition of thermodynamic fluctuations

That fluctuations are an intrinsic and inherent part and parcel of physical and natural reality is – indeed – common knowledge. Every observable (say, O) is – one way or the other – associated with some kind of random fluctuation (here-and-after denoted, δO). These fluctuations that we are talking about are different from the fluctuations in the measurement induced by random statistical human error. These are fluctuations that will manifest even when the impossible feat of reducing the intrinsic and inherent random statistical human error to zero.

In deeper terms, these fluctuations are no ordinary fluctuations encountered in statistics, but are intrinsic and inherent *Statistical Random Thermodynamic Fluctuations* (SRTF), they can not be eliminated even in the most idea of situations. These thermodynamic fluctuations are the quantum mechanical fluctuations that Niels Henrik David Bohr (1885-1962) and his followers in Copenhagen, Denmark envisaged (or dreamt of) in their historic, spirited and concerted effort to finding a meaningful, perdurable and lasting interpretation of Schrödinger's seemingly arcane quantum mechanical wavefunction Ψ .

About these thermodynamic fluctuations, we must hasten and categorically state that while there exists theories that attempt to explain the evolution of thermodynamic systems (in Γ -space), there does not exist similar attempts to describe the evolution of these SRTFs though some structured space as phase space. The present section makes an endeavour at such a feat.

3.2 Definition of the $\delta\Gamma$ -space

Now, we shall promulgate three postulates that form the basis of our theory of thermodynamic fluctuations. In the first postulate, we shall set up an arena where these fluctuations are defined. In the second postulate, we shall propose a governing equation that describes the evolution of these fluctuations on the space on which they are defined, and lastly, in the third postulate, we set up some rules that define how changes in these fluctuations relate to changes in their corresponding canonical variables.

1. **Postulate (I):** Just as there exists the six-dimensional Γ -space ($\Gamma = \Gamma(x, y, z; p_x, p_y, p_z)$) on which the trajectory of a thermodynamic system can be traced via their evolution through this space as dictated to and governed by Liouville's theorem, there exists a corresponding six-dimensional space (which for our purposes, we shall call $\delta\Gamma$ -space) on which the trajectory of the statistical random thermodynamic fluctuations ($\delta x, \delta y, \delta z; \delta p_x, \delta p_y, \delta p_z$) can be traced.
2. **Postulate (II):** The dynamic and spatial evolution of these random statistical thermodynamic fluctuations ($\delta x, \delta y, \delta z; \delta p_x, \delta p_y, \delta p_z$) on $\delta\Gamma$ -space is governed by Liouville's equation $d(\delta\varrho)/d(\delta t) = 0$, i.e.:

$$\frac{\partial(\delta\varrho)}{\partial(\delta t)} + \sum_{j=1}^N \delta\vec{v}_j \cdot \frac{\partial(\delta\varrho)}{\partial(\delta\vec{r}_j)} + \sum_{j=1}^N \delta\dot{\vec{p}}_j \cdot \frac{\partial(\delta\varrho)}{\partial(\delta\vec{p}_j)} = 0. \quad (4)$$

3. **Postulate (III):** The partial differential elements of the canonical four-position ($\partial x, \partial y, \partial z, \partial t$) and that of the canonical four-momentum ($\partial p_x, \partial p_y, \partial p_z, \partial E$) are equal to the corresponding partial differential elements of the statistical random thermodynamic fluctuations ($\partial(\delta x), \partial(\delta y), \partial(\delta z), \partial(\delta t)$) for the four-position and ($\partial(\delta p_x), \partial(\delta p_y), \partial(\delta p_z), \partial(\delta E)$) for the four-momentum – i.e. written explicitly:

$$\begin{aligned} \partial t &= \partial(\delta t) \\ \partial x &= \partial(\delta x) \\ \partial y &= \partial(\delta y) \\ \partial z &= \partial(\delta z) \\ \partial E &= \partial(\delta E) \\ \partial p_x &= \partial(\delta p_x) \\ \partial p_y &= \partial(\delta p_y) \\ \partial p_z &= \partial(\delta p_z). \end{aligned} \quad (5)$$

With these three postulates (rules), we will go on to show that the Liouville Eq. (4) yields the FLT.

4 Derivation – First Law of Thermodynamics

With the theory governing the SRTFs having been set up in the previous section, we realise that if we are to set $\delta\varrho$ so that it is defined:

$$\delta\varrho = \exp\left(\frac{\delta S_{TD}}{\hbar}\right), \quad (6)$$

where \hbar is Planck's normalized constant and:

$$\delta S_{TD} = \sum_{j=1}^N (\delta\vec{p}_j \cdot \delta\vec{r}_j - \delta E_j \delta t_j), \quad (7)$$

is the thermodynamic phase (or thermodynamic action) defined on $\delta\Gamma$ -space, then one can very easily demonstrate that Liouville's theorem as defined in (4), is actually a subtle statement of the FLT. This thermodynamic phase has been defined along the lines of the space of a particle in the Hamilton–Jacobi theory (e.g. [3, pp.490-491]) of particles where the energy E and momentum \vec{p} of a partial are related to the particle's phase S (or action) via the equation $E = -\partial S/\partial t$ and $\vec{p} = \vec{\nabla} S$. These Hamilton–Jacobi definitions of E and \vec{p}

are the defining equations in the de Broglie-Bohm Pilot Wave Theory [4–7] of Quantum Mechanics (QM).

Now, with the idea in mind that $\delta\mathcal{S}_{TD}$ is the thermodynamic phase (action) similar to a particle's phase (action) in the Hamilton–Jacobi theory, it is clear from the explicit definition of $\delta\mathcal{S}_{TD}$ given in (7), that:

$$-\frac{\partial(\delta\mathcal{Q})}{\partial(\delta t)} = \sum_{j=1}^N \delta E_j = \delta E, \quad (8)$$

$$\frac{\partial(\delta\mathcal{Q})}{\partial(\delta\vec{r}_j)} = \delta\vec{p}_j, \quad (9)$$

$$\frac{\partial(\delta\mathcal{Q})}{\partial(\delta\vec{p}_j)} = \delta\vec{r}_j. \quad (10)$$

From these equations – i.e. (8), (9) and (10), it follows that*:

$$\sum_{j=1}^N \delta\vec{v}_j \cdot \frac{\partial\mathcal{Q}}{\partial(\delta\vec{r}_j)} = \sum_{j=1}^N \vec{v}_j \cdot \frac{\partial\mathcal{Q}}{\partial(\delta\vec{r}_j)} = \sum_{j=1}^N \vec{v}_j \cdot \delta\vec{p}_j. \quad (11)$$

At this point before we can proceed, we must ask the question: *What does the term $\vec{v}_j \cdot \delta\vec{p}_j$ represent?* For a clue, let us consider the classical expression for the kinetic energy of particle $K_j = p_j^2/2m$. Clearly $dK_j = p dp/m = v_j dp_j = \vec{v}_j \cdot d\vec{p}_j$. Therefore, the expression $\vec{v}_j \cdot \delta\vec{p}_j$ represents that thermodynamic induced fluctuations in the kinetic energy of the j^{th} particle constituting the thermodynamic system under consideration. These thermodynamic induced fluctuations in the kinetic energy $\vec{v}_j \cdot \delta\vec{p}_j$ constitute what we normally call or refer to as the internal energy δU of a thermodynamic system, hence:

$$\delta U = \sum_{j=1}^N \delta\vec{v}_j \cdot \frac{\partial\mathcal{Q}}{\partial\vec{r}_j} = \sum_{j=1}^N \delta U_j. \quad (12)$$

Further, we have:

$$\sum_{j=1}^N \delta\vec{F}_j \cdot \frac{\partial\mathcal{Q}}{\partial(\delta\vec{p}_j)} = \sum_{j=1}^N \delta\vec{F}_j \cdot \delta\vec{r}_j = \sum_{j=1}^N \vec{F}_j \cdot \delta\vec{r}_j. \quad (13)$$

Clearly, the expression[†] $\vec{F}_j \cdot \delta\vec{r}_j$, needs no explanation as it represents the work δW_j done on the j^{th} particle by the random thermodynamic fluctuations of position and forces, i.e.:

$$\delta W = \sum_{j=1}^N \delta\vec{F}_j \cdot \frac{\partial\mathcal{Q}}{\partial\vec{p}_j} = \sum_{j=1}^N \delta W_j. \quad (14)$$

From all this, it follows that:

$$\delta E = \delta U + \delta W. \quad (15)$$

*The “ δ ” in $\delta\vec{v}_j$ in (11) is removed via the definitions given in (5).

†The “ δ ” in $\delta\vec{F}_j$ is removed via the definitions given in (5).

What (15) is telling us that while the fluctuations are random, they are correlated.

Now, for a system that moves from an initial state (i) to a final state (f), where the changes in the thermodynamic fluctuations ($\delta E, \delta U, \delta W$) are to be defined:

$$\begin{aligned} dQ &= \delta E_f - \delta E_i \\ dU &= \delta U_f - \delta U_i \\ dW &= \delta W_f - \delta W_i, \end{aligned} \quad (16)$$

where dQ, dU and dW , are to have the same meaning as they have in (1), it follows from this that we will have the FLT, the meaning of which is that Liouville's theorem (4) is, in this way, a subtle expression of the FLT.

5 Discussion

As far as we can tell, the FLT is taken as an inviolable experimental fact. There has not been – at least in our survey of the literature, a similar attempt as that presented here where a fundamental theoretical basis is made to furnish the foundations of this law, hence, this work is without precedent insofar as its nature and goal is concerned. We believe the attempt presented herein is important for our deeper insight and understanding of the *Science of Thermodynamics*. The follow-up work (briefly discussed in Section 7) that we will present soon will attest to this.

For example, one may ask: *What drives thermodynamics, it is the direct changes in the canonical values of the internal energy U and the work W , or there – perhaps – is something else different from this?* If what we have presented is to be believed, then the answer is that thermodynamics is driven by the changes in the associated SRTFs in the canonical values of the internal energy U and the work W , that is to say, by $d(\delta U) = \delta U_f - \delta U_i$ and $d(\delta W) = \delta W_f - \delta W_i$. In a nutshell, it is the SRTFs that drive thermodynamics, and not the changes dU and dW .

6 Conclusion

Assuming the acceptability of what has herein been presented, we hereby set the following as our conclusion:

1. From a fundamental theoretical standpoint, the First Law of Thermodynamics may very well be an expression to the effect that the Thermodynamic Evolution Probability Density Function $\delta\mathcal{Q}$ is – in accordance with Liouville's theorem – an explicit time-constant along the phase-space trajectory for any thermodynamic system.
2. Liouville's Theorem can be viewed as (or may very well be) an expression of the First Law of Thermodynamics.

7 Follow-up work

In order for the effectiveness in its mission to deliver the core message it seeks to deliver, it is always prudent to keep a paper focused on the point on which it seeks to deliver – of which, the present has been to demonstrate that Liouville's

theorem can be shown to be a casting of the FLT. As always happens, there will always be follow-ups. At present, we have three immediate follow-up papers that we hope will be published in the present journal. These follow-up papers give further credence to the ideas that we have herein crafted and used to demonstrate that Liouville's theorem can be envisaged as a casting of the FLT.

1. In the first follow-up paper, we demonstrate that if $\delta\varrho$ is assumed to be a thermodynamic probability measure, then one can derive – with relative ease – Heisenberg (1927)'s quantum mechanical uncertainty principle [8].
2. In the second paper, which is a follow-up on our recent work presented in [9] on “A Simple Proof of the Second Law of Thermodynamics (SLT)”, we demonstrate that – if $\delta\varrho$ is assumed to be the thermodynamic probability that derives entropy changes in thermodynamic systems, then for a Universe with a unidirectional forward arrow of time, the SLT directs that energy and time fluctuations ($\delta E, \delta t$) are what derives thermodynamics.
3. Lastly, in the third paper, within the framework of the de Broglie-Bohm Pilot Wave Theory [4–7] of QM, commonly referred to as *Bohmian Mechanics* (BM), we set the square-root of the Schrödinger [10–12] quantum mechanical probability amplitude $\Psi^*\Psi = |\Psi|^2$ so that it equals $\delta\varrho$, i.e. $\delta\varrho = |\Psi|$, in which event, we demonstrate that all the criticism that has been levelled against BM – since its inception in 1952 – can easily be overcome. The importance of this is that it allows for a realistic interpretation of QM. This is good for the philosophy of QM.

We believe that all the above mentioned future works give *seminality* to the ideas here set forth.

Received on October 19, 2019

References

1. Holton G. and Elkana Y. Albert Einstein, Historical and Cultural Perspectives. Princeton University Press, Princeton, NJ, 2016. (ISBN 978-0-691-64026-6).
2. Liouville J. Sur la Théorie de la Variation des Constantes Arbitraires. *Journ. de Math.*, 1838, v. 3, 342–349.
3. Goldstein H. Classical Mechanics, 2nd edition. Addison-Wesley, Reading, MA, 1980. (ISBN: 978-0-201-02918-5).
4. de Broglie L. XXXV. A Tentative Theory of Light Quanta. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 1924, v. 47 (278), 446–458.
5. Bohm D. J. A Suggested Interpretation of the Quantum Theory in Terms of “Hidden” Variables. I. *Phys. Rev.*, 1952, v. 85, 166–179.
6. Bohm D. J. A Suggested Interpretation of the Quantum Theory in Terms of “Hidden” Variables. II. *Phys. Rev.*, 1952, v. 85, 180–193.
7. Bohm D. J. Proof That Probability Density Approaches $|\psi|^2$ in Causal Interpretation of the Quantum Theory. *Phys. Rev.*, 1953, v. 89, 458–466.
8. Heisenberg W. K. Ueber den anschaulichen Inhalt der Quantentheoretischen Kinematik and Mechanik. *Zeitschrift für Physik*, 1927, v. 43 (3), 172–198. English Translation: Wheeler J. A. and Zurek W. H, eds. Quantum Theory and Measurement. Princeton University Press, Princeton, NJ, 1983, pp. 62–84.
9. Nyambuya G. G. A Simple Proof of the Second Law of Thermodynamics. *Progress in Physics*, 2019, v. 15 (3), 171–177.
10. Schrödinger E. An Undulatory Theory of the Mechanics of Atoms and Molecules. *Phys. Rev.*, 1926, v. 28, 1049–1070.
11. Schrödinger E. Quantisierung als Eigenwertproblem. *Annalen der Physik*, 1926, v. 384 (4), 361–376.
12. Schrödinger E. Quantisierung als Eigenwertproblem. *Annalen der Physik*, 1926, v. 385 (13), 437–490.