

# Mechanical Proof of the Second Law of Thermodynamics Based on Volume Entropy

Michele Campisi

*Department of Physics, University of North Texas, P.O. Box 311427, Denton, TX  
76203-1427, USA*

---

## Abstract

In a previous work (M. Campisi. *Stud. Hist. Phil. M. P.* 36 (2005) 275-290) we have addressed the mechanical foundations of equilibrium thermodynamics on the basis of the Generalized Helmholtz Theorem. It was found that the volume entropy provides a good mechanical analogue of thermodynamic entropy because it satisfies the heat theorem and it is an adiabatic invariant. This property explains the “equal” sign in Clausius principle ( $S_f \geq S_i$ ) in a purely mechanical way and suggests that the volume entropy might explain the “larger than” sign (i.e. the Law of Entropy Increase) if non adiabatic transformations were considered. Based on the principles of microscopic (quantum or classical) mechanics here we prove that, provided the initial equilibrium satisfy the natural condition of decreasing ordering of probabilities, the expectation value of the volume entropy cannot decrease for arbitrary transformations performed by some external sources of work on a insulated system. This can be regarded as a rigorous quantum mechanical proof of the Second Law. We discuss how this result relates to the Minimal Work Principle and improves over previous attempts. The natural evolution of entropy is towards larger values because the natural state of matter is at positive temperature. Actually the Law of Entropy Decrease holds in artificially prepared negative temperature systems.

*Key words:* quantum adiabatic theorem, minus first law, negative temperature, minimal work, Helmholtz theorem, arrow of time.

---

## 1 Introduction

This work addresses the problem of explaining the Second Law of Thermodynamics on the basis of the microscopic laws of mechanics. As discussed earlier

---

*Email address:* [campisi@unt.edu](mailto:campisi@unt.edu) (Michele Campisi).

(Campisi, 2005) the Second Law of thermodynamics is commonly understood as composed of two parts which we shall conventionally label as “part A” and “part B”. “Part A” is essentially a statement about the *Existence of Entropy*. It says that there exists an integrating factor  $\frac{1}{T}$ , interpreted as inverse temperature, such that  $\frac{\delta Q}{T}$  is an exact differential, where  $\delta Q = dE + PdV$  is the heat exchanged during a very small variation of the thermodynamic state  $(E, V)$ . This implies that there exists a function of the thermodynamic state, the entropy  $S$ , that generates the exact differential

$$dS = \frac{\delta Q}{T}. \quad (1)$$

“Part A” of the second Law evidently pertains to *equilibrium thermodynamics*. Its mechanical foundations have been studied in a previous work (Campisi, 2005). The main conclusion drawn in that work was that the laws of ergodic Hamiltonian mechanics alone are sufficient for providing a rather satisfactory explanation of this part of the Second Law. The approach adopted was that of establishing a correspondence between the *thermodynamic* quantities  $E, P, T, V$  and certain suitably chosen time-averaged *mechanical* quantities. Thanks to a generalization of Helmholtz Theorem, then we were able to find the proper *mechanical analogue* of thermodynamic entropy. This is the so called *Volume Entropy*:

$$S_{\Phi}(E, V) = \ln \int_{H(\mathbf{q}, \mathbf{p}; V) \leq E} \frac{d^{3N} \mathbf{q} d^{3N} \mathbf{p}}{h^{3N}} \quad (2)$$

where  $H(\mathbf{q}, \mathbf{p}; V)$  is the system’s Hamilton function. This is a function of the  $6N$  dimensional phase-space vector  $\mathbf{q}, \mathbf{p}$  and the external parameter  $V$ .  $h$  is an arbitrary constant with the dimensions of action.

The present contribution completes the previous one by addressing “Part B” of the Second Law. “Part B” is essentially the Law of Entropy increase, and as such is a statement that pertains to *non-equilibrium thermodynamics*. To avoid any possible confusion, here by “Part B” of the Second Law and “Law of Entropy increase”, we mean Clausius formulation of the Entropy Principle (Uffink, 2001):

THE ENTROPY PRINCIPLE: For every *nicht umkehrbar* process in a thermally isolated system which begins and ends in an equilibrium state, the entropy of the final state is greater than or equal to that of the initial state. For every *umkehrbar* process in a thermally isolated system the entropy of the final state is equal to that of the initial state

The expressions *nicht umkehrbar* and *umkehrbar* could be translated into the current scientific English as *non quasi static* and *quasi static* respectively. It must be stressed that the Entropy Principle refers to transformations caused by the variation of some external field, and is not at all a statement about the

*spontaneous tendencies* of physical systems. If the variation of the external field is acted in such a way as to drive the system out of equilibrium (non quasi static process) the entropy will increase. If it is acted in such a way that the system will remain arbitrary close to equilibrium (quasi static process) then the entropy will not change.

Indeed the volume entropy already well accounts for the “quasi static” part of the Entropy Principle. In facts, as it is known since the work of Hertz (1910), the volume entropy is an *ergodic adiabatic invariant*. Namely a quantity that does not change during a quasi-static transformation of the external field. As pointed out in (Campisi, 2005), the laws of ergodic Hamiltonian mechanics alone provide a quite satisfactory explanation of the “quasi static” part of the Entropy Principle: no statistics is needed to explain the equal sign in the Entropy Principle. It must be emphasized that here we are establishing a correspondence between the thermodynamic concept of quasi static process and the classical mechanical concept of adiabatic transformation. In particular the expression “adiabatic” will not be used as synonym of “thermally insulated” as customarily happens in Thermodynamics text-books.

Obviously the fact that the Volume Entropy well accounts for “part A” and the quasi static part of “part B” of the Second Law, suggests that it might turn out to be very useful in addressing the non quasi static part of “part B”. Simple considerations suggest that the latter could be proved only in some statistical or averaged sense, though. Consider for example a 1D particle of mass  $m$  in a 1D box of length  $L$ . The particle bounces forth and back inside the box. Let  $E$  be the energy of the particle. Imagine that we can change to length of the box by moving the right wall of the box. The volume entropy of this elementary ergodic system is simply  $S_{\Phi}(E, L) = \ln(2L\sqrt{2mE})$ . Now imagine that we perform a very fast compression of the box, much faster than the particle period of motion  $T = \sqrt{\frac{m}{2E}}L$ . Let  $L - \Delta L$  be the final length of the box. Imagine that during this transformation the particle is far from the moving wall and does not bounce against it. Its energy would not change but the change of its volume entropy would be  $\Delta S_{\Phi} = \ln(1 - \Delta L/L)$ . Namely it would be negative. This simple argument should convince that any purely mechanical attempt to prove the Entropy Principle on the basis of Volume Entropy would be vain. We certainly need to add some statistical ingredient if we want to prove it.

Thus we are going to assume that the initial energy of our insulated system is not known. All we know is that it is within some range  $E, E + dE$  with some probability  $p(E)\Omega(E)dE$ . The symbol  $\Omega(E)$  denotes the “density of states” at energy  $E$ .  $\Omega(E)$  is also named surface integral (Campisi, 2005) or structure function (Khinchin, 1949). For example, if we first place the system in thermal contact with a heat bath at temperature  $T$ , and then we remove the contact, we will not know for certain what the energy of the system will be, but we

will know that  $p(E) = \frac{e^{-E/T}}{Z}$ .

In this work we will prove that, provided that  $p(E)$  is a decreasing function of  $E$ , the *expectation value* of the Volume Entropy will be larger than its initial one. It turns out that such proof is much easier in quantum mechanics rather than classical mechanics. Therefore we shall first quantize the Volume Entropy and then study its behavior under the action of a varying field, that is a time-dependent perturbation.

The paper is organized as follows. In Sec. 2 we introduce the quantum counterpart of the classical volume entropy. In Sec. 3 we prove that the expectation value of such quantum operator can only increase, if the initial conditions is represented by a decreasing ordering of probabilities. In Sec. 4 we discuss how this result relates to Thomson's formulation of the second Law, whereas in Sec. 5 we compare the quantum volume entropy with other quantum entropies present in the literature. In Sec. 6 we show how to adapt the quantal proof of Sec. 3 to the classical case. The role of the initial equilibrium is discussed in Sec. 7. We will discuss the fact that the results proven in the paper are direct consequences of the time-reversal symmetric microscopic laws, and that, besides the law of entropy increase, there exists a law of entropy decrease as well. The conclusions are drawn in Sec. 8.

## 2 Quantum Volume Entropy

Let us first consider the 1D case. In 1D the volume entropy reads:

$$S_{\Phi} = \ln \int_{H \leq E} \frac{dx dp}{h}. \quad (3)$$

This can be conveniently reexpressed as the logarithm of the *reduced action* (Landau and Lifshitz, 1960)

$$S_{\Phi} = \ln \oint \frac{p dx}{h}. \quad (4)$$

This is also known as the Helmholtz Entropy (Campisi, 2005). Quantization of the Helmholtz Entropy is almost immediate. Indeed, using a colorful expression, I would say that Eq. (4) invites the reader to quantize. Using the semiclassical approximation of Bohr-Sommerfeld (Landau and Lifshitz, 1958) and setting  $h$  equal to Plank's constant allows to see that  $S_{\Phi}$  is a quantized quantity whose possible values are (within the range of validity of the approximation):

$$S_{\Phi} = \ln \left( n + \frac{1}{2} \right) \quad (5)$$

We can extend this reasoning to multidimensional systems whose dynamics is ergodic. In this general case the Volume Entropy is given by Eq. (2). Again using the quasi-classical viewpoint (Landau and Lifshitz, 1978) the integral in Eq. (2) approximately counts the number of quantum states not above a certain energy  $\varepsilon_n = E$ . Since the levels are non degenerate this number is  $n + \frac{1}{2}$ , where one considers that the vacuum state counts as a half state. The levels are non-degenerate because the corresponding classical dynamics is ergodic. This can be understood by noticing that ergodicity implies that the Hamiltonian is the only integral of motion. This, translated into the language of quantum mechanics, says that the Hamiltonian alone constitute a complete set of commuting observables, so that the only quantum number is  $n$ .

At this point, it is quite easy to construct the quantum version of Volume Entropy. Consider a finite (i.e., not necessarily macroscopic) *non-degenerate* quantum systems. Let  $\mathcal{N}$  be the *quantum number operator*, i.e.:

$$\mathcal{N} \doteq \sum_{k=0}^K k |k\rangle \langle k| \quad (6)$$

where  $\{|k\rangle\}$  is the complete orthonormal set of Hamiltonian's eigenstates.  $K$ , the total number of energy levels, can be infinite. The eigenvectors of  $\mathcal{N}$  are the energy eigenvectors, and the eigenvalues are the corresponding quantum numbers. Then the *Quantum Volume Entropy Operator* can be defined as:

$$\mathcal{S} \doteq \ln \left( \mathcal{N} + \frac{1}{2} \right) \quad (7)$$

We adopt a system of units where  $k_B$ , Boltzmann constant, is equal to 1.

### 3 Proof of the Entropy Principle

Armed with a quanta-mechanical analogue of thermodynamic entropy (7), we can now study its evolution under a time-dependent perturbation. As prescribed by the Entropy Principle we shall assume that the system is thermally isolated from the environment. As discussed previously, the system energy is not known. This means that the system is assumed to be in a statistical mixture of states, described by a density matrix  $\rho_i$ , rather than a pure state  $|k\rangle$ . As prescribed by the Entropy Principle we shall also assume that the system be initially at equilibrium. We will translate this thermodynamic notion into the quantal requirement that  $\frac{\partial \rho_i}{\partial t} = 0$ . So the system is at equilibrium whenever  $\frac{\partial \rho}{\partial t} = 0$  and it is out of equilibrium whenever  $\frac{\partial \rho}{\partial t} \neq 0$ . At  $t = t_i$ , we switch on a perturbation. This is implemented by changing the value of some external parameter  $\lambda$  during the course of time:  $\lambda = \lambda(t)$ .  $\lambda$  can be for example the volume  $V$  of a vessel containing the system, or the value of some external

field like an electric or a magnetic field. At time  $t = t_{off}$ , the perturbation is switched off. We assume that at some time  $t_f \geq t_{off}$  any transient effect will be vanished and the system attains a new equilibrium state described by some  $\rho_f$ , such that  $\frac{\partial \rho_f}{\partial t} = 0$ . Thus, before time  $t_i$  and after  $t_f$ , the system is at equilibrium, and for  $t_i < t < t_f$  it is out of equilibrium. Due to the perturbation the Hamiltonian changes from the initial value  $H_i$  to the final value  $H_f$ , and accordingly the quantum entropy operator will change in time and move from  $\mathcal{S}_i$  to  $\mathcal{S}_f$ . We introduce the following time-dependent orthonormal basis set  $\{|k, t\rangle\}$ . The vectors  $|k, t\rangle$  are defined as the eigenvectors of the “frozen” Hamiltonian  $\overline{H}_t \doteq H(t)$ . That is:

$$H(t) = \sum_{k=0}^K \varepsilon_k(t) |k, t\rangle \langle k, t| \quad (8)$$

Since at time  $t_i$   $\frac{\partial \rho_i}{\partial t} = 0$ , then  $[\rho_i, H] = 0$ . This means that  $\rho_i$  is diagonal over the initial basis  $\{|k, t_i\rangle\}$ :

$$\rho(t_i) = \sum_{k=0}^K p_k |k, t_i\rangle \langle k, t_i| \quad (9)$$

As anticipated in the introduction we shall assume that  $p_i$  is decreasing:

$$p_0 \geq p_1 \geq \dots \geq p_i \geq \dots \quad (10)$$

Our definition of quantum entropy (7), is essentially an *equilibrium* definition. Using the bases  $\{|k, t\rangle\}$ , we can extend the definition to the *out of equilibrium* case, as following:

$$\mathcal{S}(t) \doteq \sum_{k=0}^K \ln \left( k + \frac{1}{2} \right) |k, t\rangle \langle k, t| \quad (11)$$

We shall assume that non-degeneracy is kept at all times. This implies that there is *no level crossing*, and ensures that the quantum number operator gives the correct eigenvalues at all times. The same assumption is used by Allahverdyan and Nieuwenhuizen (2005) to ensure the proper ordering of energy eigenvalues. Note that, unlike the Hamiltonian’s spectrum (8), the spectrum of the quantum entropy (11) is time-independent. We define the transition probabilities:

$$|a_{kn}(t_f)|^2 = |\langle n, t_f | U(t_i, t_f) | k, t_i \rangle|^2 \quad (12)$$

Where

$$U(t_i, t) = \mathcal{T} \exp \left( -\frac{i}{\hbar} \int_{t_i}^t H(s) ds \right) \quad (13)$$

is the time evolution operator expressed in terms of the time-ordered exponential  $\mathcal{T} \exp$ . The  $|a_{kn}(t_f)|^2$ ’s represent the probabilities that the system will be found in the state  $|n, t_f\rangle$  at time  $t_f$  provided that it was in the state  $|k, t_i\rangle$  at

time  $t_i$ . They satisfy the relations (Allahverdyan and Nieuwenhuizen, 2005):

$$\sum_{k=0}^K |a_{kn}(t_f)|^2 = \sum_{n=0}^K |a_{kn}(t_f)|^2 = 1 \quad (14)$$

and

$$|a_{kn}(t_f)|^2 \geq 0 \quad (15)$$

For the change in the expectation value of the quantum entropy  $\mathcal{S}$  of Eq. (7) we have:

$$S_f - S_i = Tr [\rho_f \mathcal{S}_f] - Tr [\rho_i \mathcal{S}_i] = \sum_{n=0}^K (p'_n - p_n) \ln \left( n + \frac{1}{2} \right) \quad (16)$$

where

$$p'_n = \sum_{k=0}^K p_k |a_{kn}(t_f)|^2 \quad (17)$$

is the probability that the system is in state  $|n, t_f\rangle$  provided that the initial probabilities were  $p_n$ .

Using the ‘‘summation by parts’’ rule (Allahverdyan and Nieuwenhuizen, 2005):

$$\sum_{n=0}^K a_n b_n = a_K \sum_{n=0}^K b_n - \sum_{m=0}^{K-1} (a_{m+1} - a_m) \sum_{n=0}^m b_n \quad (18)$$

Eq. (16) becomes

$$S_f - S_i = \sum_{m=0}^K \ln \frac{m + \frac{3}{2}}{m + \frac{1}{2}} \sum_{n=0}^m (p_n - p'_n) \quad (19)$$

We have:

$$\begin{aligned} \sum_{n=0}^m (p_n - p'_n) &= \sum_{n=0}^m p_n - \sum_{n=0}^m \sum_{i=0}^K p_i |a_{in}(t_f)|^2 \\ &= \sum_{n=0}^m p_n \left( 1 - \sum_{i=0}^m |a_{in}(t_f)|^2 \right) - \sum_{n=0}^m \sum_{i=m+1}^K p_i |a_{in}(t_f)|^2 \end{aligned} \quad (20)$$

From Eq.s (14) and (15) we have  $(1 - \sum_{i=0}^m |a_{in}(t_f)|^2) \geq 0$  and  $|a_{in}(t_f)|^2 \geq 0$ , therefore using the ordering of probabilities (10) we get (see also (Allahverdyan and Nieuwenhuizen, 2005)):

$$\sum_{n=0}^m (p_n - p'_n) \geq p_m \sum_{n=0}^m \left( 1 - \sum_{i=0}^m |a_{in}(t_f)|^2 \right) - p_m \sum_{n=0}^m \sum_{i=m+1}^K |a_{in}(t_f)|^2 \quad (21)$$

$$= mp_m - p_m \sum_{n=0}^m \sum_{i=0}^K |a_{in}(t_f)|^2 = 0 \quad (22)$$

where we used Eq. (14) in the last line. Noting that  $\ln \frac{m+\frac{3}{2}}{m+\frac{1}{2}} > 0$  in Eq. (19), we finally reach the conclusion that:

$$S_f \geq S_i \quad (23)$$

This inequality holds for any transformation acted on a thermally insulated, non degenerate quantum system which is initially at equilibrium with a decreasing ordering of probabilities. To complete the proof of the Entropy Principle we have to prove that the equal sign holds for adiabatic transformation. Note that the non-degeneracy assumption ensures that the *quantum adiabatic theorem* holds (Messiah, 1962). This ensures that the transition probability between states with different quantum number will be null during an adiabatic transformation:

$$|a_{in}(t_f)|^2 = \delta_{in} \quad (24)$$

Therefore, for an adiabatic transformation we get  $p'_i = p_i$  (see Eq. 17), which brings to

$$S_f = S_i \quad (25)$$

This concludes our quanta-mechanical proof of the Entropy Principle. Note that the result in Eq. (25) is not surprising because the quantum entropy operator has been defined as the quantum counterpart of a classical adiabatic invariant.

Also note that we have established and used the following correspondences between thermodynamics and quantum mechanics:

- entropy  $\Leftrightarrow \ln \left( \mathcal{N} + \frac{1}{2} \right)$
- equilibrium  $\Leftrightarrow \frac{\partial \rho}{\partial t} = 0$
- (non)quasi-static process  $\Leftrightarrow$  (non)adiabatic perturbation

Since the equilibrium condition for the final state has never been used in the proof, inequality (23) holds for any  $t \geq t_i$ . Note that this by no means implies that

$$S(t) \doteq Tr[\mathcal{S}(t)\rho(t)] \quad (26)$$

is a monotonic increasing function of time. All we can say is that if at times  $t_1 < t_2 < \dots < t_n < \dots$  the density matrix is diagonal and its spectrum is monotonic decreasing, then:

$$S(t_1) \leq S(t_2) \leq \dots \leq S(t_n) \leq \dots \quad (27)$$

In general there can well be two times  $t_A < t_B$ , where for example the system is out of equilibrium, such that  $S(t_A) > S(t_B)$ . It is important to stress that, when the system is out of equilibrium the quantity  $S(t)$  shouldn't be regarded as the system's thermodynamic entropy, which is essentially an equilibrium property. Thus  $S(t)$  is only one of the many possible out of equilibrium gen-



eralizations of entropy. What makes it special is that it proves effective in addressing the Entropy Principle.

#### 4 Thomson's formulation and the Minimal Work Principle

The present proof of The Entropy Principle is very close, in the approach and methods, to a result discussed recently by Allahverdyan and Nieuwenhuizen (2002). They considered the following alternative formulation of the Second Law, which they attribute to Kelvin (W. Thomson):

THOMSON'S FORMULATION: No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source.

If we denote the work done by the external source as  $W$ , the principle can be expressed simply as:

$$W \geq 0 \quad (28)$$

The proof of Allahverdyan and Nieuwenhuizen (2002) goes like the one we have proposed above for the Entropy Principle. Indeed that work has been a major source of inspiration for the present one. In this case one wants to study the following quantity:

$$W \doteq Tr[H_f \rho_f] - Tr[H_i \rho_i] \quad (29)$$

for a cyclic process. This means that the final Hamiltonian is assumed to be equal to the initial one  $H_f = H_i \doteq H_0$ . Thus:

$$W \doteq \sum_{n=0}^K \varepsilon_n (p'_n - p_n) \quad (30)$$

where  $\varepsilon_n$  are the eigenvalues of  $H_0$ . These are ordered according to  $\varepsilon_1 < \varepsilon_2 < \dots < \varepsilon_i < \dots$ . The eigenvalues  $\varepsilon_n$ , play here the same role as the entropy eigenvalues  $\ln(n + 1/2)$ , in Eq. (16). Thus it is immediate to see that, under the assumption of decreasing probabilities (10), Eq. (28) holds quantum-mechanically.

In a subsequent work Allahverdyan and Nieuwenhuizen (2005) have extended this result to the case of possibly non cyclic transformation. They have found that

$$W - \widetilde{W} = \sum_{n=0}^K \varepsilon'_n (p'_n - p_n) \geq 0 \quad (31)$$

Where  $\varepsilon'_n$  are the eigenvalues of the final Hamiltonian,  $W$  is the work actually performed on the system and  $\widetilde{W}$  is the work that would have been performed

if the same transformation would have been carried adiabatically. The proof is formally equivalent to the one discussed here. Eq. (31) expresses the Minimal Work Principle according to which, whenever we perform a non-adiabatic transformation, we spend more work than we would have if performing an adiabatic one.

The formal similarity of Eq. (31) and Eq. (16) proves that the formulation of the Second Law as a Principle of Minimal Work or as an Entropy Principle are *equivalent*. In particular it is easily seen that:

$$\text{sign}(W - \widetilde{W}) = \text{sign}(S_f - S_i) \quad (32)$$

Thus the two principles are equivalent. Further, whenever one is violated, the other will be too. Cases where the Minimal Work Principle is violated because of level crossing are discussed by Allahverdyan and Nieuwenhuizen (2005). In those case The Entropy Principle would be violated too.

The history behind this kind of quanta-mechanical proofs of the Second Law is relatively recent, and can be traced back at least to the works of Lenard (1978) and Bassett (1978). Due to the lack of a suitable quanta-mechanical analogue of entropy, though, the application of such quantal approaches has remained restricted to the analysis of statements that concern work, whose mechanical definition is quite straightforward. To the best of the author's knowledge, similar arguments and approaches have been previously proposed for addressing the Entropy Principle only in the relatively un-known work of Tasaki (2000). Tasaki already proposed the quantum entropy operator in the form  $\mathcal{S} = \ln \mathcal{N}$ , but the connection with the Generalized Helmholtz Theorem (which has been introduced later (Campisi, 2005)) was not made, neither the importance of the volume entropy as a good mechanical analogue of thermodynamic entropy for possibly low dimensional systems was recognized. Unlike the present work, in fact, the work of Tasaki (2000) is concerned only with the macroscopic case.<sup>1</sup>

## 5 Comparison with other quantum entropies

The employment of the Quantum Volume Entropy improves quite a lot over previous attempts at explaining the Entropy Principle based on quantum entropies. In fact, the employment of the entropy in Eq. (26) has many advantages over other quantum mechanical entropies present in literature. In

---

<sup>1</sup> The work of Tasaki (2000) contained a simultaneous proof of both Eq. (23) and Eq. (31). It is interesting to notice that Tasaki did not published his result because Eq. (31) was proven previously by Lenard (1978). To the best of my knowledge, the proof of Eq. (23) based on the logarithm of the principal quantum number was never given before though, thus it remained unpublished.

contrast with von Neumann entropy:

$$S_{vN} = -Tr[\rho(t) \ln \rho(t)]. \quad (33)$$

the expectation value of the quantum operator  $\mathcal{S}$  does change in time, and it has been proved to increase under the assumption discussed. Tolman's coarse-grained entropy (Tolman, 1938):

$$S_{cg}(t) = -\sum_{\nu} P_{\nu}(t) \ln P_{\nu}(t) \quad (34)$$

does change in time and it is an adiabatic invariant (Tolman, 1938). Nonetheless it fails in accounting for the inequality sign in the case of non-adiabatic perturbations. All we know is that for an infinitesimal *abrupt* transformation that begins and ends in a *canonical equilibrium* the corresponding change in  $S_{cg}$  is non-negative (Tolman, 1938). But this does not ensure that for any *finite* non-adiabatic transformation the change would be non-negative as required by Clausius formulation. Tolman's argument according to which any finite transformation could be reproduced by a sequence of many infinitesimal abrupt transformations each followed by the reaching of a canonical equilibrium does not seem to be tenable. In fact, as a result of a finite non-adiabatic transformation, the system could well end up in a non-canonical distribution (Allahverdyan and Nieuwenhuizen, 2005). Further, Tolman's definition of entropy of Eq. (34) applies only to macroscopic equilibrium systems. On the contrary the result proved in Sec. 3 holds *no matter the number of degrees of freedom* of the system. Thus the Quantum Volume Entropy might turn out to be very useful in the novel and fast growing field of *Quantum Thermodynamics* of nanoscale systems. See for example (Nieuwenhuizen et al., 2005), see also (Kieu, 2004).

## 6 Classical case

The result of Eq. (23) can be proved also classically. Let the system be initially distributed according to some probability distribution function  $p_0(E)$ . Let  $p_1(E)$  be the final distribution. Let  $\Phi_0(E)$  and  $\Phi_1(E)$  denote the volumes enclosed by the hyper-surfaces  $H_0(\mathbf{q}, \mathbf{p}) = E$  and  $H_1(\mathbf{q}, \mathbf{p}) = E$  respectively. Where  $H_0$  and  $H_1$  are the initial and final Hamiltonians. The volume entropy of a representative point that at time  $t_i$  lies on the hyper-surfaces  $H_0(\mathbf{q}, \mathbf{p}) = E$  is  $\ln \Phi_0(E)$ . We have a similar expression for time  $t_f$ . Then:

$$S_f - S_i = \int_0^{\infty} dE \Omega_1(E) p_1(E) \ln \Phi_1(E) - \int_0^{\infty} dE \Omega_0(E) p_0(E) \ln \Phi_0(E) \quad (35)$$

where  $\Omega_r$  denotes the initial ( $r = 0$ ) or final ( $r = 1$ ), structure function. Note that in general

$$dE\Omega_r(E) = d\Phi_r(E) \quad (36)$$

Thus we can make the change of variable  $E \leftrightarrow \Phi_r$  in the integrals. Let  $P_r(\Phi_r) \doteq p_r(E(\Phi_r))$ , then we have (after dropping the subscript in  $\Phi_r$ ):

$$S_f - S_i = \int_0^\infty d\Phi (P_1(\Phi) - P_0(\Phi)) \ln \Phi \quad (37)$$

This is the classical analogue of Eq. (16). The role of  $n + \frac{1}{2}$  is played by the “enclosed volume”  $\Phi$ , and the discrete probabilities  $p_n, p'_n$  are now probability density functions  $P_r(\Phi)$ . Since the evolution is deterministic, it is possible to express the final probability in terms of the initial one as

$$P_1(\Phi) = \int_0^\infty d\Theta A(\Phi, \Theta) P_0(\Theta) \quad (38)$$

where  $A(\Phi, \Theta)$  is the Green function associated to the evolution of probabilities in  $\Phi$  space. That is  $A(\Phi, \Theta)$  represents the evolved at time  $t_f$  of a Dirac delta centered around  $\Theta$  at time  $t_i$ . If we denote the time evolution operator that evolves probabilities in  $\Phi$  space from time  $t_i$  to time  $t_f$  as  $\mathcal{U}$ ,  $A$  is defined as:

$$A(\Phi, \Theta) = \mathcal{U} \delta(\Phi - \Theta) \quad (39)$$

The function  $A(\Phi, \Theta)$  is the classical counterpart of the transition probability  $|a_{kn}|^2$ . Evidently, thanks to the classical adiabatic theorem we have for an adiabatic switching:

$$A(\Phi, \Theta) = \delta(\Phi - \Theta) \quad (40)$$

This is the classical counterpart of Eq. (24). For non adiabatic switching we expect  $A(\Phi, \Theta)$ , considered as a function of  $\Phi$ , to be bell-shaped with some finite width. The problem of determining the shape of  $A$  has been studied by Jarzynski (1992), who proved that, within the second order of adiabatic perturbation theory,  $A$  actually drifts and diffuses according to an effective Fokker-Planck equation. Since  $A(\Phi, \Theta)$  represents a probability distribution function in  $\Phi$  space, it satisfies:

$$A(\Phi, \Theta) \geq 0 \quad (41)$$

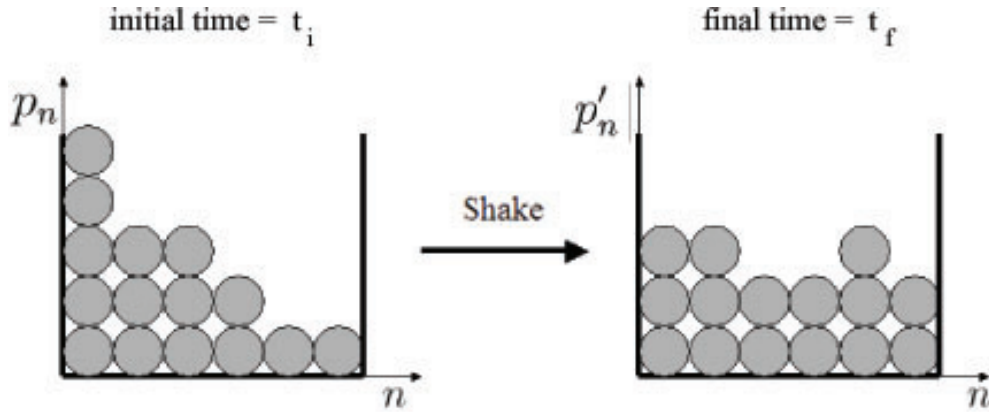
and

$$\int_0^\infty d\Phi A(\Phi, \Theta) = 1 \quad (42)$$

Using Liouville’s Theorem it is also possible to prove that:

$$\int_0^\infty d\Theta A(\Phi, \Theta) = 1. \quad (43)$$

The analogy with the quantum case has been completely established now, and the proof of the Entropy Principle follows by repeating the same steps.



$$S_i = \langle \ln(n + 1/2) \rangle_i \leq \langle \ln(n + 1/2) \rangle_f = S_f$$

Fig. 1. Visual representation of the effect of a non adiabatic perturbation on a quantum system which is initially described by decreasing probabilities. After shaking, the initial accumulation towards the left would flatten out, and the average value of  $\ln(n + 1/2)$  (i.e. the entropy) would increase.

The requirement on the initial distribution  $P_0(\Phi)$  is that it be a decreasing function of  $\Phi$ . Since  $\Phi_0(E)$  is increasing, this requirement translates into the requirement that  $p_0(E)$  be a decreasing function of  $E$ .

## 7 The role of the initial equilibrium

Inequality (23) holds as a direct consequence of the time reversal symmetric microscopic laws of quantum or classical mechanics. As such, it does not entail any arrow of time. The reason for the emergence of the  $\geq$  sign in Eq. (23) should be looked for, rather, in the fact that we have considered only a certain restricted subset of all possible initial conditions. To explain this point it might be useful to see our ensemble of systems as a box containing many balls (see Fig. 1). Each ball represents an element of the ensemble. The box is divided into labelled cells that represent the quantum states. The cell most close to the left wall is state with  $n = 0$ , its right neighbor cell is the state  $n = 1$  and so forth. At time  $t_i$ , the balls are distributed in the box according to some probability  $p_n$ . We can see the time dependent perturbation acted on the system as the action of shaking the box. The effect of the shaking is that of flattening out the initial distribution. Thus if initially we had some accumulation of balls towards the left side of the box, we expect the final state to be more flat. If we look at the average value of  $n$  or any other increasing function of  $n$ , like for example  $\ln(n + 1/2)$ , we would record an increase of such values. This is a mere consequence of the fact that initially we had an accumulation towards the left. If initially we have had an accumulation towards

the right, again the shaking would flatten out the distribution, but this time we would see a decrease of the average value of  $n$  and of  $\ln(n + 1/2)$ . If instead the initial distribution were flat, we would see no change in those quantities. Indeed it is quite easy to see that the sign of inequality (23) would be reversed if an increasing ordering of initial probability is assumed. Therefore, for such subset of the set of all possible initial distributions, we actually have a Law of Entropy Decrease! This reflects the fact that there is no asymmetry in the time evolution of the Volume Entropy operator. Thus, in principle, it should be possible to observe a decrease of entropy if the initial equilibrium would be given by an *inverted population*. In other words, we should be able to observe an inverted Second Law of Thermodynamics in *Negative Temperature* systems. Indeed experimental evidence of this exists since the very pioneering works of Pound, Purcell and Ramsey on spin systems (Pound, 1951; Purcell and Pound, 1951; Ramsey and Pound, 1951; Ramsey, 1956). They observed that

“when a negative temperature spin system was subjected to resonance radiation, more radiant energy was given off by the spin system than was absorbed (Ramsey, 1956)”

This means that it is possible to extract work from a negative temperature system by means of a cyclic transformation. In other words, for negative temperature systems we already have experimental evidence that:

$$W \leq 0 \tag{44}$$

Because of the *equivalence* of the Minimal Work Principle and the Entropy Principle, in this case we would also have:

$$S_f \leq S_i \tag{45}$$

The fact that the Law of Entropy Increase is overwhelmingly more often observed than its symmetrical Law of Entropy Decrease is a consequence of the fact that positive temperatures are overwhelmingly more common than negative ones. The former in fact is the *natural* state of matter, whereas the second can only be created *artificially* and only in few very special cases. Ramsey (1956) already pointed out that very strict conditions must be met for a system to be capable of negative temperatures: (a) the system must be at equilibrium (b) there must be an upper limit in the Hamiltonian’s spectrum (c) the system must be thermally isolated from the environment. The second requirement is very restrictive as most systems have an unbounded kinetic energy term in the Hamiltonian<sup>2</sup>. Also the requirement (c) is restrictive in the sense that thermal insulation can be achieved only approximately and for

---

<sup>2</sup> See (Mosk, 2005) for a recent and interesting example of negative kinetic temperature, though.

a certain amount of time. On the contrary the inevitable thermal contact of our system with its environment would eventually bring it to the monotonic decreasing Gibbs state

$$p_i = Z^{-1}e^{-\beta\varepsilon_i}, \quad (46)$$

The latter describes the natural state of matter, and as such is the *inevitable* initial condition of any thermodynamic experiment<sup>3</sup>. Thus the time asymmetry of the laws of thermodynamics arises at the level of the initial thermal equilibrium, rather than in the Second Law itself. This seems to be in agreement with the view expressed by Brown and Uffink (2001), according to which the Second Law does not entail any time asymmetry. The origin of the arrow of time should be looked for, instead, in the Minus First Law of thermodynamics, namely the *Equilibrium Principle* (Brown and Uffink, 2001).

## 8 Conclusion

Adopting an approach similar to those adopted previously to prove the Thomson's formulation of the Second Law, here we have proved the Entropy Principle on the basis of Quantum Mechanics, for initial conditions characterized by decreasing probabilities. This completes a programme devoted to the study of the mechanical foundations of Thermodynamics initiated with a previous work (Campisi, 2005). That work addressed the equilibrium part of the Second Law, whereas the present one addresses the out of equilibrium part. The key tool of investigation adopted in both studies is the Volume Entropy. Here we have compared it to other quantum entropies and shown that it proves more effective in addressing the Entropy Principle. We discussed the equivalence of the Entropy Principle and Thomson's Principle and have seen that the Entropy Principle can be proved classically as well. The apparent time asymmetry expressed by the Second Law stems from the fact that initial decreasing probabilities are overwhelmingly more common and natural in ordinary experimental set-ups than increasing ones. Indeed a Reversed Entropy Principle can be observed in artificially prepared negative temperature systems.

## References

Allahverdyan, A. E., Nieuwenhuizen, T. M., 2002. A mathematical theorem as the basis for the second law: Thomson's formulation applied to equilibrium. *Physica A* 305 (3-4), 542–552.

---

<sup>3</sup> If we consider that in experiments on negative temperature systems one has first to create an inverted population from a natural one, we will see that indeed the total entropy change would be positive. The entropy spent to create the inverted population is larger than that gained back when applying the resonant radiation.

- Allahverdyan, A. E., Nieuwenhuizen, T. M., 2005. Minimal work principle: Proof and counterexamples. *Phys. Rev. E* 71 (4), 046107.
- Bassett, I. M., 1978. Alternative derivation of the classical second law of thermodynamics. *Phys. Rev. A* 18 (5), 2356–2360.
- Brown, H. R., Uffink, J., 2001. The origins of time-asymmetry in thermodynamics: The minus first law. *Studies In History and Philosophy of Modern Physics* 32 (4), 525–538.
- Campisi, M., 2005. On the mechanical foundations of thermodynamics: The generalized Helmholtz theorem. *Studies In History and Philosophy of Modern Physics* 36, 275–290.
- Hertz, P., 1910. Über die mechanischen Grundlagen der Thermodynamik. *Annalen der Physik* 33 (Leipzig), 225–274 and 537–552.
- Jarzynski, C., 1992. Diffusion equation for energy in ergodic adiabatic ensembles. *Physical Review A* 46, 7498–7509.
- Khinchin, A., 1949. *Mathematical foundations of statistical mechanics*. Dover, New York.
- Kieu, T. D., 2004. The second law, maxwell’s demon, and work derivable from quantum heat engines. *Physical Review Letters* 93 (14), 140403.
- Landau, L., Lifshitz, E., 1958. *Quantum mechanics, non-relativistic theory*. Pergamon, London.
- Landau, L., Lifshitz, E., 1960. *Mechanics*. Pergamon, Oxford.
- Landau, L., Lifshitz, E., 1978. *Statistical Physics, I*. Pergamon, Oxford.
- Lenard, A., 1978. Thermodynamical proof of the gibbs formula for elementary quantum systems. *J. Stat. Phys* 19, 575.
- Messiah, A., 1962. *Quantum Mechanics*. North Holland, Amsterdam.
- Mosk, A. P., 2005. Atomic gases at negative kinetic temperature. *Physical Review Letters* 95 (4), 040403.
- Nieuwenhuizen, T., Keefe, P., Špicka, V. (Eds.), 2005. *Frontiers of Quantum*. Vol. 29 of *Physica E*.
- Pound, R. V., 1951. Nuclear spin relaxation times in single crystals of lif. *Phys. Rev.* 81 (1), 156.
- Purcell, E. M., Pound, R. V., 1951. A nuclear spin system at negative temperature. *Phys. Rev.* 81 (2), 279–280.
- Ramsey, N. F., 1956. Thermodynamics and statistical mechanics at negative absolute temperatures. *Phys. Rev.* 103 (1), 20–28.
- Ramsey, N. F., Pound, R. V., 1951. Nuclear audiofrequency spectroscopy by resonant heating of the nuclear spin system. *Phys. Rev.* 81 (2), 278–279.
- Tasaki, H., 2000. Statistical mechanical derivation of the second law of thermodynamics. [arXiv:cond-mat/0009206](https://arxiv.org/abs/cond-mat/0009206).
- Tolman, R. T., 1938. *The Principles of Statistical Mechanics*. Oxford University Press, London.
- Uffink, J., 2001. Bluff your way in the second law of thermodynamics. *Studies in History and Philosophy of Modern Physics* 32 (3), 305–394.