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Clarifying the link between von Neumann and thermodynamic entropies

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Abstract. The state of a quantum system being described by a density operator ρ , quantum statistical mechanics calls the quantity $-k\text{Tr}(\rho \ln \rho)$, introduced by von Neumann, its von Neumann or statistical entropy. A 1999 Shenker's paper initiated a debate about its link with the entropy of phenomenological thermodynamics. Referring to Gibbs's and von Neumann's founding texts, we replace von Neumann's 1932 contribution in its historical context, after Gibbs's 1902 treatise and before the creation of the information entropy concept, which places boundaries into the debate. Reexamining von Neumann's reasoning, we stress that the part of his reasoning implied in the debate mainly uses thermodynamics, not quantum mechanics, and identify two implicit postulates. We thoroughly examine Shenker's and ensuing papers, insisting upon the presence of open thermodynamical subsystems, imposing us the use of the chemical potential concept. We briefly mention Landau's approach to the quantum entropy. On the whole, it is shown that von Neumann's viewpoint is right, and why Shenker's claim that von Neumann entropy "is not the quantum-mechanical correlate of thermodynamic entropy" can't be retained.

1 Preliminary considerations

In Quantum Statistical Mechanics (QSM), S , the (statistical) entropy of a system described by a density operator ρ is given by the von Neumann (VN) expression $S_{VN} = -k \langle \ln \rho \rangle$ (k : Boltzmann constant) [von Neumann 1932; Landau 1958]. The spectrum of the ρ eigenvalues is strictly discrete [von Neumann 1932; Messiah 1965] and, summing over a basis of ρ eigenstates, with corresponding eigenvalues w_j , the reduced entropy is:

$$\sigma_{VN} = \frac{S_{VN}}{k} = -\text{Tr}(\rho \ln \rho) = -\sum_j w_j \ln w_j. \quad (1)$$

Eq. (1) is also used in the presently developing Quantum Information Processing field, σ_{VN} being called the von Neumann information entropy [Nielsen 2000].

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The *time evolution* of the density operator $\rho(t)$ for an isolated system with deterministic Hamiltonian H obeys the Liouville-von Neumann equation $i\hbar d\rho/dt = [H, \rho]$, and its VN entropy is then time-independent, since:

$$-\frac{d\sigma_{VN}}{dt} = \text{Tr}\left(\frac{d\rho}{dt} \ln \rho\right) = \frac{1}{i\hbar} \text{Tr}([H, \rho] \ln \rho) = \frac{1}{i\hbar} \text{Tr}([\rho, \ln \rho]H) = 0. \quad (2)$$

Small parts of the Hamiltonian of macroscopic quantum statistical systems are often unknown, which is possibly described with a random Hamiltonian. The evolution of σ_{VN} (cf. e.g. [Balian 1982, p. 104]) is then related to the temporal increase of entropy in isolated macroscopic systems (second law of thermodynamics). This difficult question, discussed since Boltzmann, first in a classical context, is still open, as shown by recent contributions from J. Lebowitz, in a classical [Lebowitz 2007] or quantum [Lebowitz 2007; Lebowitz 2010] context. The present paper is *not* devoted to this time evolution.

At *thermal equilibrium*, there is a consensus that in Classical Statistical Mechanics (CSM) Gibbs entropy corresponds to the entropy of thermodynamics (from now on an abbreviation for phenomenological thermodynamics). About Gibbs entropy, Jaynes e.g. wrote: "once we accept the established proposition that the Gibbs ensemble does yield the correct equilibrium thermodynamics, then there is logically no room for any assumption about which quantity represents entropy: it is a question of mathematically demonstrable fact" [Jaynes 1965]. This consensus also exists in the quantum case, as verified e.g. by reading the first chapter of Feynman's concise book entitled *Statistical mechanics* [Feynman 1972]. This chapter, an introduction to equilibrium QSM, clearly shows that the VN expression is a brick in building up equilibrium QSM, with the introduction of the thermodynamic quantities and the establishment of relations between them.

In 1999, a paper by Shenker [Shenker 1999] raised some doubt about this consensus upon the relation between the VN statistical entropy and the entropy of thermodynamics. His paper generated a reply from Henderson [Henderson 2003] criticizing Shenker's arguments and conclusion, followed by a paper from Hemmo and Shenker [Hemmo 2006] moving the debate into multiple directions. These three papers are restricted to equilibrium situations (anyway, in off-equilibrium situations, one can't speak of the entropy of thermodynamics, but only at best introduce a local thermodynamic entropy [Callen 1966]). Since Shenker's paper, its conclusion has somewhat diffused within the Philosophy of Science field (cf. e.g. Ch. 7 of [Hagar 2004]). Our examination of VN's approach as suggested by Shenker's paper led us to set [Shenker 1999] into a broader perspective, presented in this paper.

The entropy concept is now used in quite distinct fields, which explains the appearance of the interdisciplinary journal *Entropy* in 1999, and may explain why the three above-mentioned papers appeared in journals devoted to the Philosophy of Science. It seems undoubtful that "in the last forty years, philosophy of physics has become a large and vigorous branch of philosophy" [Butterfield 2007, Introduction, p. XIII]. And, concerning the second law, Jaynes spoke of an "enormous *conceptual* difficulty". But the content of [Shenker 1999; Henderson 2003; Hemmo 2006] forced us to pay attention to the choice and right use of adequate physical concepts, and to their historical development.

Concerning the choice and use of concepts, we will e.g. stress that the chemical potential concept is a tool for finding the equilibrium states of *open* thermodynamical (sub)systems, and will try to establish whether, when Shenker claims that, "if S_{VN} is entropy, then perpetual motion machines are possible" [Shenker 1999], his claim respects the general principles of physics.

Concerning the historical development of concepts and ideas in physics, it is helpful, in the context of our subject, to identify the radical change in the introduction

of the idea of entropy in the field of QSM, when comparing VN's approach with that adopted today e.g. in [Balian 1982]. Between VN and Balian, [Shannon 1948] initiated the development of modern Information Theory, and allowed Jaynes to start a presentation of the foundations of both CSM and QSM by introducing the entropy through the concept of information rather than from thermodynamics. This will have two consequences for us: 1) Peres (cf. Subsection 3.3) agrees with VN about the significance of VN entropy, but, although he refers to VN's mental experiment to be soon described, he gets his conclusion through a quite distinct path, 2) for clarity and for an economy of thought and space, we limit the present paper to an examination of the path followed by VN. A right appreciation of that historical evolution in the presentation of the foundations of QSM is favoured by a thorough examination of the canonical texts [Gibbs 1902] and [von Neumann 1932] (we henceforth use the first edition of its English translation). [Dirac 1930] and [von Neumann 1932] are generally seen as the synthetic treatises which stabilized the foundations of quantum theory after the 1924-1927 years. But this fame may hide the fact that VN's book also generalized the description of macroscopic systems by statistical mechanics, made by Gibbs in a classical context, to a quantum one.

[Hemmo 2006] largely uses different *interpretations* of quantum mechanics (QM), as opposed to the *laws* of QM. Such a use presents several difficulties: 1) the number of interpretations is not low, and their use may make the discussion quite technical and specialized, 2) differences appearing in the conclusions from two distinct interpretations could arise from the interpretations and not from the laws of QM, 3) the debate may deviate towards a discussion between those who, as Fuchs and Peres, estimate that "quantum theory needs no interpretation" [Fuchs 2000], and those who reply: "Quantum Theory: Interpretation Cannot be Avoided" [Denis 2004]. But we will see that: 1) the part of VN's reasoning under discussion mainly uses thermodynamics, 2) VN's reasoning uses a relation involving the quantum system which is implicitly postulated, 3) several quantum results established by VN were accepted up to now in the debate initiated by [Shenker 1999]. When referring to QM, these last facts stimulate us to try and keep to its laws and to avoid additional specific interpretation and/or possible philosophical implication of that interpretation.

In Section 2, we recall the definition and some properties of the entropy used by thermodynamics. Then, in Section 3, we present and comment the introduction of the statistical entropy in [von Neumann 1932]. Section 4 is devoted to a critical examination of [Shenker 1999; Henderson 2003; Hemmo 2006], the main papers involved in that debate. A short presentation of QSM by [Landau 1958], which introduces VN's definition of entropy without any use of VN's justification, is provided in Section 5. Sections 6 and 7 are respectively devoted to a short discussion and to the conclusion.

2 Thermodynamic entropy

Clausius introduced the concept of entropy by postulating that, in an infinitesimal reversible transformation where the thermal energy exchange of the system (at temperature T) with the external world is DQ_r , then DQ_r/T is a total differential denoted dS , S being called the (thermodynamic) entropy of that system. The notation DQ , from [Kittel 1969], stresses the presence of a differential form, as opposed to a total differential. Systems first considered were closed (no matter exchange). The extension to open systems (presence of matter exchange), was made by Gibbs [Gibbs 1875; Gibbs 1902], who introduced the concept of chemical potential and the corresponding matter exchange internal energy term. In this paper, we follow the canonical book [Callen 1966] as it adopts a systematic postulational approach of thermodynamics

and moreover does not ignore open systems. Callen first restricts his attention to specific macroscopic systems which he calls simple (excluding e.g. systems with surface effects). For them, the existence of the general principle of energy conservation (for an isolated system) is reflected in the postulate of the existence of an energy function, the internal energy U , additive over the constituent subsystems. Callen then introduces particular states of these simple systems, called equilibrium states. For a simple system, an equilibrium state is completely defined by specifying its internal energy U , its volume V , and the mole numbers $n_1 \dots n_i$ of its chemical components. Callen then postulates the existence of a function $S(U, V, n_1 \dots n_i)$ (fundamental relation) defined for these equilibrium states, called entropy, additive over independent subsystems, homogeneous of degree one versus $U, V, n_1 \dots n_i$ (cf. [Jaynes 1992; Balian 1982, p. 159]), differentiable, and monotonously increasing with U . It is postulated that whenever internal constraints in an isolated system (neither energy nor matter exchange) are suppressed, the system spontaneously comes into a new equilibrium state where its entropy has the maximum value compatible with the remaining constraints. For a system with an entropy function $S(U, V, n)$, e.g. a single phase of a single fluid, the total differential has the form [Callen 1966, Sec. 2.1]:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dn, \quad (3)$$

where T is the temperature of the system, P the pressure and μ the chemical potential. For an ideal gas with temperature-independent heat capacity at constant pressure \mathcal{C}_P (and therefore at constant volume \mathcal{C}_V too), the chemical potential of n moles with internal energy U and volume V is (cf. Appendix B):

$$\frac{\mu}{T} = R \ln \frac{U^{\frac{1}{1-\gamma}} V^{-1} n^{\frac{\gamma}{\gamma-1}}}{(U^{\frac{1}{1-\gamma}} V^{-1} n^{\frac{\gamma}{\gamma-1}})_0} + \left(\frac{\mu}{T}\right)_0, \quad (4)$$

where T is the temperature of the gas, $\gamma = \mathcal{C}_P/\mathcal{C}_V$, and the index 0 refers to an arbitrary reference state.

When there are two chemical species, each in a given phase (e.g. neon and krypton in the gaseous state), with n_1 and n_2 moles respectively, there are two chemical potentials, μ_1 and μ_2 [Callen 1966, Sec. 2.1].

In order to introduce results which will be useful in the following Sections, we now imagine a model isolated cylinder, separated by an internal wall into two parts with respective volumes V_1 and V_2 . Initially, the internal wall is adiabatic, rigid and firmly fixed, impermeable to matter, and each part is in an equilibrium state, with respectively n_1 and n_2 moles of the same gas, ideal or not, at respective temperatures T_1 and T_2 . At some instant, the internal wall becomes both diathermal (thermal exchanges become allowed) and permeable to the gas. In the final equilibrium state, as a result of entropy extremalization respecting the remaining constraints, the gas in parts 1 and 2 has the same temperature and **the same chemical potential** [Callen 1966, Sec. 2.8]. If now the gas is an ideal gas verifying (4), because of these equalities then V/n has the same value in the two regions, and since $PV = nRT$ (cf. Appendix A), the pressure has the same value in the two parts. This equality of the final pressures is *not* a priori verified, as the internal wall is permanently rigid and fixed. Thermodynamically treating that final equilibrium without explicit or implicit use of the chemical potential concept would mean considering each part of that isolated system as *closed* whereas each part is *open* (cf. Appendix B).

Some frustration, well identified in [Kittel 1969], is generally felt when starting the study of thermodynamics, which postulates the existence of the entropy function S , and simultaneously declares that it is unable to give any microscopic interpretation of

S , since it operates strictly at the macroscopic level. When Boltzmann and Gibbs built (classical) statistical mechanics, they aimed at getting a microscopic interpretation of the principles of thermodynamics, and particularly of S . Today, thermodynamics as deduced from the principles of (quantum or classical) statistical mechanics is called *statistical thermodynamics*, as opposed to (*phenomenological*) *thermodynamics*, which rests on a few postulates operating at the macroscopic level. Paraphrasing [Callen 1966, p. 267], one should admit that the point of division between thermodynamics and statistical mechanics can be displaced towards statistical mechanics, if new postulates, suggested by results from statistical mechanics, are introduced into thermodynamics, which e.g. allows a "thermodynamic theory of fluctuations" to be built. We will ignore this possible extension of thermodynamics, which would be a possible source of confusion for the question under examination.

It should be clear that thermodynamics, while using rather abstract language and construction, is however a natural science, since: 1) its general principles, and concepts such as temperature or pressure, were suggested by experience, 2) it makes full use of the principle of energy conservation, historically suggested by experience (cf. [Poincaré 1902, Ch. 8; Poincaré 1908; Sommerfeld 1950]), 3) an aim of thermodynamics is to get information upon a physical system already partly experimentally known: e.g. the Reech formula (Landau 1958, (16.14)) allows us to know a thermal quantity by measuring mechanical quantities only.

3 Von Neumann and statistical entropy

Statistical mechanics explicitly takes the microscopic constituents into account, describing them with a more or less realistic model. CSM is now considered an approximation of QSM, valid in some limiting conditions (classical regime: cf. [Kittel 1969] and footnote ¹). This point should not be understood *stricto sensu*, since CSM considers that the atoms or molecules of a gas are distinguishable, whereas QM has taught us that they are not. In the case of gases, it then happens that when comparing the theoretical expressions obtained in the classical regime and the corresponding ones valid in CSM, the same expression is obtained for the internal energy U , but the expressions for the entropy S differ (Gibbs paradox [Kittel 1969]), the correct one being given by QSM. In the context of this paper, one has to refer first to [Gibbs 1902] upon CSM, since VN explicitly refers to Gibbs in [von Neumann 1932].

In order to correctly appreciate VN's justification of his expression for entropy (S_{VN}) in [von Neumann 1932], one must replace it in this larger context. It is then essential to identify the existence, content *and order* of three distinct parts: 1) in Sec. 2 of Ch. 5, VN first introduces the concept of quantum semi-permeable walls, and shows that they may separate orthogonal and only orthogonal states. **He then establishes his expression for S_{VN} , the entropy of a quantum system.** 2) in Sec. 3, VN proves that a quantum measurement is irreversible, and, using his expression for the entropy, he derives expressions for a quantum system *at thermal equilibrium (QSM)* which are formally identical to those found by Gibbs for a classical system (CSM) in [Gibbs 1902]. 3) Ch. 6 is devoted to the quantum measuring process.

¹ At temperature T , when quantum particles obey Bose or Fermi statistics, $\bar{n}(\varepsilon)$, the mean number of quantum particles in a quantum state with energy ε , is $\bar{n}(\varepsilon) = 1/(e^{(\varepsilon-\mu)/kT} \pm 1)$ (+ for bosons, - for fermions, μ : chemical potential). If these identical independent particles are in such experimental conditions that, for any energy ε , the inequality $e^{(\varepsilon-\mu)/kT} \gg 1$ holds, then $\bar{n}(\varepsilon) \simeq e^{-(\varepsilon-\mu)/kT}$ for any ε . It therefore appears that the expression for $\bar{n}(\varepsilon)$ is then identical to that of the classical Maxwell-Boltzmann statistics, and the system of particles is said to be in the classical regime [Kittel 1969]. But the particles are then still indistinguishable, contrary to their classical counterparts, and this has important consequences in entropy considerations.

3.1 Von Neumann and Gibbs

In the introduction of [Gibbs 1902], Gibbs defines statistical mechanics as "a branch of mechanics which owes its origin to the desire to explain the laws of thermodynamics on mechanical principles", which he does in Ch. 14, entitled "Discussion of thermodynamical analogies". If the physical system of interest ("the system") Σ is modeled with n pointlike particles obeying the laws of classical mechanics, its state at some instant t is described, in the Hamiltonian formalism, by the collection of its $6n$ coordinates and momenta $(q_1, q_2, \dots, q_{3n}, p_1, p_2, \dots, p_{3n})$. Gibbs introduces (p. 5) an abstract space with $6n$ dimensions associated with (q_1, \dots, p_{3n}) , its *phase space* Γ . The state of the system at time t is represented by a point M in Γ . As time evolves, M follows a trajectory in Γ , according to the $6n$ corresponding Hamilton equations. But this trajectory can't be known, since the initial position of M in Γ and parts of the Hamiltonian are experimentally unknown and uncontrollable. As a consequence, if the same experiment or measurement is repeated several times, keeping the same macroscopic conditions, the results will slightly differ in these successive experiments. This suggests introducing the concept of probability by mentally repeating the same experiment with Σ . Gibbs instead introduces a mental collection $\Sigma_1, \Sigma_2, \dots, \Sigma_N$ of systems (*ensemble of systems*, today called a Gibbs ensemble [Gibbs 1902, preface; Penrose 1979]), each system being a copy, or replica, of Σ obeying the same mechanical laws as Σ , but differing in its initial conditions and Hamiltonian while respecting the same macroscopic constraints as Σ . The number of these replica $N \rightarrow \infty$ [Gibbs 1902, note in p. 5] in such a way that the corresponding points in Γ may be regarded as distributed continuously within Γ . Gibbs then introduces ρ , the probability density in phase space (noting it P and calling it the *coefficient of probability*): the probability for Σ of being represented by a point within a volume $d\Gamma$ around M in Γ at t is $\rho(M, t)d\Gamma$.

In Ch. 1 of [Gibbs 1902], Gibbs establishes several properties verified by ρ . In Ch. 4, he discusses the form to be taken by ρ at statistical equilibrium (defined as a situation where ρ is time-independent), which leads him to propose the canonical law as "the most simple case conceivable". His expression contains two constants, Ψ and Θ , which gain a meaning in Ch. 14, when Gibbs establishes the link with thermodynamics, the canonical law becoming:

$$\rho = \frac{e^{-\beta E}}{\int_{\Gamma} e^{-\beta E} d\Gamma}, \quad (5)$$

where the energy E is a function of the $6n$ coordinates of M , and the denominator allows for normalization. The physical system of interest is weakly coupled to another system of far greater heat capacity, acting as at thermostat and imposing that system its temperature T , and $\beta = 1/kT$. Gibbs also introduces the natural logarithm of ρ , which he calls the index of probability and denotes η . He establishes that $-\bar{\eta}$, the mean value of $-\eta = -\ln \rho$, corresponds to the (reduced) thermodynamic entropy:

$$-\bar{\eta} = -\langle \ln \rho \rangle = -\int_{\Gamma} \rho \ln \rho d\Gamma, \quad (6)$$

with ρ given by (5). One should be careful that, e.g. in (116) of [Gibbs 1902], $-\bar{\eta}$ is denoted as η , i.e. as the index of probability. Today's notation for $-\bar{\eta}$ is S_G/k (Gibbs reduced entropy). In Ch. 11, Gibbs establishes several properties verified by S_G . He particularly proves that, when mentally varying ρ with given mean energy, the expression for ρ making S_G maximum is the canonical law. Eq. (6) is a generalization

of a relation first postulated by Boltzmann, written as $S_B = k \ln W$ since Planck, W being the number of "complexions" (roughly: microscopic states) realizing a given "macroscopic state". That relation from Boltzmann bridged the gap between thermodynamics and statistical mechanics. In that relation and in (6), k , the Boltzmann constant, is a scale factor allowing compatibility between the predictions of CSM and experimental facts.

In [Gibbs 1902], Gibbs also establishes general expressions showing that the major thermodynamic quantities can be deduced from the knowledge of the partition function $Z = \int_{\Gamma} e^{-\beta E} d\Gamma$. One may e.g. write U (cf. the explanation following his relation (484)) and the reduced entropy S_G/k (cf. the expression of $d\Psi/d\Theta$ after his relation (251)) as:

$$U = -\frac{\partial}{\partial\beta} \ln Z, \quad (7)$$

$$\frac{S_G}{k} = [\beta U + \ln Z]. \quad (8)$$

In Ch. 5 of [von Neumann 1932], VN explicitly refers to Gibbs in Sec. 2, writing "we are dealing with a Gibbs ensemble" (cf. also his notes 185 and 186). And, in the second part of the next section, the discussion starting with "we shall now investigate the stationary equilibrium superposition, i.e., the mixture of maximum entropy when the energy is given", is the quantum version of Gibbs's work. Von Neumann then introduces the partition function and establishes that (7) and (8) are still valid with quantum macroscopic systems. He then stresses that: 1) "the analogy of the expressions obtained above for the entropy, equilibrium ensemble etc., with the corresponding results of the classical thermodynamical theory is striking" (p. 395), 2) the quantum statistical mixture which he uses at thermal equilibrium contains the weight $e^{-W/kT}$, and "the classical "canonical" ensemble is defined in exactly the same way" (p. 397).

In the *classical* case, in (6), ρ has the same dimensions as $d\Gamma^{-1}$, i.e. the dimensions (action) $^{-3n}$ with a system of n point-like particles. It is known that, rather than $\ln \rho$, one should therefore write $\ln (\rho \xi^{3n})$ where ξ is some well-chosen constant of the dimensions of action, which suggests that this question is linked to the choice of the origin of entropy. In the *quantum* case, the phase space is not used, the ρ spectrum is discrete, and this question does not appear. We will not discuss this point (cf. [Jaynes 1992; Balian 1982, Ch. 3]).

3.2 Von Neumann's justification for S_{VN}

When care is taken of considering the whole treatment of equilibrium QSM by von Neumann (cf. the beginning of our Section 3), it can picturesquely be said that VN first uses thermodynamics *to guess* the expression for quantum entropy in Sec. 2 of Ch. 5 of [von Neumann 1932], entitled "thermodynamical considerations", and that he then inserts this expression in Sec. 3, in his building of QSM. The final justification of his whole work upon QSM is found in the subsequent historical confrontation of his theoretical results with experimental reality (Sackur-Tetrode relation: cf. Section 7). In this paper, we focus upon these "thermodynamical considerations", essential for the work undertaken in [Shenker 1999; Henderson 2003; Hemmo 2006], examined in our Section 4.

In Sec. 2 of [von Neumann 1932], with \mathbf{S} , the quantum system, VN associates mental replicas $\mathbf{S}_1 \dots \mathbf{S}_N$ ($N \gg 1$), an approach agreeing both with his previous introduction of the concept of statistical mixture in Ch. 4 of [von Neumann 1932],

and with the Gibbs ensemble method. Each replica is strictly uncoupled to any other replica (cf. his note 186). VN then links each replica to a molecule of an ideal gas: 1) each system \mathbf{S}_i is (mentally) enclosed in a massive, impenetrable box K_i , all the boxes $K_1 \dots K_N$ being themselves in a quite large, massive box \bar{K} coupled to a heat reservoir, which imposes its temperature T to \bar{K} and to the boxes K_i (but not to their contents \mathbf{S}_i), 2) Quantum system \mathbf{S} is described by a density operator ρ_Q , which may reduce to a projector $P_{|\varphi\rangle} = |\varphi\rangle\langle\varphi|$ (the mixed state then reduces to the pure state $|\varphi\rangle$). Having introduced an orthonormal basis $\{|\varphi_n\rangle\}$ of the state space of \mathbf{S} , we will consider that when the state of \mathbf{S} is described by $\rho_Q = \sum_n w_n P_{|\varphi_n\rangle}$, then in this discussion everything happens as if $w_n N$ among the N replicas were in the state $|\varphi_n\rangle$, and this for any n , i.e. the frequency interpretation may be used for the probabilities w_n . This agrees with the discussion of the meaning of a statistical mixture previously given by VN, in [von Neumann 1932, Ch. 4 Sec. 1], where VN examines two interpretations.

VN calls each box K_i a *molecule*, and system \mathbf{S}_i inside box K_i an *internal degree of freedom* of molecule i . Even more briefly, one can think of this internal degree as a *spin* (of a paramagnetic molecule), remembering that the K_i are in fact generally macroscopic (as in the Gibbs ensemble method). We stress that the word "molecule" has a triple ambiguity in the present context: 1) it generally refers to a macroscopic system, 2) it may refer either to the translational motion of the box K_i (translational motion of the molecule) or to the association of the translational motion and "spin", i.e. to the box *either without or with* its content, 3) in [von Neumann 1932, Ch. 5 Sec. 2], VN writes: "... it is evident that ordinary statistics be used, and that the Bose-Einstein and Fermi-Dirac statistics... do not enter into the problem". If "molecules" are delocalized over the same volume, this does not mean that these molecules are distinguishable, as they may be distinguished only through their "spin". It rather corresponds to the idea that, because of the quite high masses and quite low concentrations of these "molecules", this gas is in the classical regime (cf. footnote ²).

One of VN's aims is to associate a specific entropy with each state of the Quantum system, i.e with each ρ_Q . This means that in each box K_i the system \mathbf{S}_i is supposed *not to be* in thermal equilibrium with the bath (through K_i and \bar{K}). And the whole procedure followed by VN means that he considers "spin" \mathbf{S}_i to be uncoupled to "(the rest of the) molecule" K_i . The situation is then the following: one has a collection of independent molecules, possibly classified into several species through their spin state. The K_i are maintained at constant temperature T ; the *spin* of each molecule *is not coupled to the other degrees of freedom of the molecule, nor to any bath*. Spins with a very weak coupling are found e.g. in nuclear magnetism (with true nuclear spins). In thermodynamics, given a thermodynamical system, its entropy is defined for all equilibrium states. This is presently true for the translational motions of the molecules, and especially when the K_i are kept at constant temperature T . **VN postulates** a generalization of that fact for any state of a quantum system, either a pure state ($\text{Tr}\rho_S^2 = 1$) or a mixed state ($\text{Tr}\rho_S^2 < 1$): **an entropy can then in principle be defined for each density operator ρ_Q** , and that therefore not depending upon the way this state appeared. Rejecting this postulate would mean giving up any hope of building a quantum version of statistical mechanics. We will call it **von Neumann's postulate 1**.

VN first shows that *all pure states have the same entropy*, which he decides to take equal to 0 (origin of entropies). He then accepts the existence of *semi-permeable*

² With ordinary atoms or molecules, the specific effects resulting from this constraint occur only at low temperature, with the lightest elements (helium and hydrogen) at high concentration (quantum liquids). Presently, the masses are far greater and the concentrations quite lower.

walls, and supplies an argument that they *can separate orthogonal states and only them* (another justification is given, within Peres's approach, in [Peres 2002]). These results were accepted in [Shenker 1999; Henderson 2003; Hemmo 2006], and will not be examined in this paper.

VN then imagines a transformation where, both in the initial and final states, all the molecules (boxes K_i) are enclosed in a volume V and at temperature T . The initial state of their spins (spin \mathbf{S} and spins of ensemble $\{\mathbf{S}_1 \dots \mathbf{S}_N\}$) is the most general mixed state, described by $\rho_Q = \sum_n w_n P_{[\varphi_n]}$, (VN denotes it U). Their final state is the pure state $|\varphi\rangle$ (ρ_Q reduces to the projector $P_{[\varphi]}$). VN evaluates the entropy changes through successive transformations between these states. The final state is clearly not a state of thermal equilibrium ($\{\mathbf{S}_1 \dots \mathbf{S}_N\}$ is in a pure state) and the same is generally true for the initial state (the state for $\{\mathbf{S}_1 \dots \mathbf{S}_N\}$ is described by an *arbitrary* ρ_Q). Such evaluations are however relevant, because: 1) the molecules (K_i) and spins (\mathbf{S}_i) being uncoupled, their entropies are additive. We will call this property for $\{K_i, \mathbf{S}_i\}$ **von Neumann's postulate 2** (thermodynamics considers the entropy S of the collection of the whole molecules $\{K_i, \mathbf{S}_i\}$, and not separately that of $\{K_i\}$ or $\{\mathbf{S}_i\}$), 2) thanks to von Neumann's postulates 1 and 2, and to the permanent thermal equilibrium of the molecules K_i at temperature T , VN is able to apply results from thermodynamics to the thermodynamic entropy variations and finally to find the expression for the entropy associated with ρ_Q .

We keep a simplification in VN's scheme made in [Shenker 1999], supposing that the density operator ρ_Q has only two eigenvalues w_1 and w_2 (Shenker moreover supposes that $w_1 = w_2 = 1/2$). The generalization to more than two eigenvalues is easy, through repetition of the process. *We moreover number the successive stages in a way making them compatible with Fig. 1 of [Shenker 1999]*, therefore starting with number 2 (in [Shenker 1999], Shenker adds number 1, with physical conditions of the molecules and of their spins identical to those in the last one, 7, to get a cycle):

2) N molecules in volume V , at T . Their spins in the mixed state $\rho_Q = (w_1 |\varphi_1\rangle\langle\varphi_1| + w_2 |\varphi_2\rangle\langle\varphi_2|)$.

4) *After reversible separation* (with intermediate states 3, cf. Appendix B): in a first box with volume V , $w_1 N$ molecules at T , their spins in state $|\varphi_1\rangle$; in a second box with volume V , $w_2 N$ molecules at T , their spins in state $|\varphi_2\rangle$.

5) After isothermal reversible compressions, the $w_1 N$ molecules in the first box occupy a volume $w_1 V$ at T , their spins being still in state $|\varphi_1\rangle$; the $w_2 N$ molecules in the second box occupy a volume $w_2 V$, at T , their spins being still in state $|\varphi_2\rangle$.

6) All the molecules have been kept in their own volume ($w_1 V$, $w_2 V$). The spins have all been quasi-statically brought to state $|\varphi\rangle$.

7) The N molecules have been brought into the same box with volume V , and kept at T , their spins being kept in the pure state $|\varphi\rangle$.

VN considers the system formed by the two *uncoupled* parts {molecules, their spins}, or more clearly {translational motions, "spins"} as a thermodynamical system. Its entropy variation in a transformation is additive (statistical independence, as suggested by uncoupling [Landau 1958], and VN's postulate 2): $\Delta S = \Delta S_{trans} + \Delta S_{spins}$.

Following VN, we consider the entropy variations of the system {translation motions, spins} from stages 2 to 7, respectively denoting $\Delta S_{trans}(i \rightarrow j)$ and $\Delta S_{spins}(i \rightarrow j)$ the entropy variations of the translation motions of the molecules and of their spins in transformation $i \rightarrow j$. We start with 2 \rightarrow 4. According to thermodynamics (cf. Appendix C) and to VN, during the 2 \rightarrow 4 reversible transformation the entropy of the system $\{K, \mathbf{S}\}$ does not change:

$$\Delta S(2 \rightarrow 4) = 0, \quad (9)$$

and therefore the "spin" entropy variation $\Delta S_{spins}(2 \rightarrow 4)$ and the translational motion entropy variation $\Delta S_{trans}(2 \rightarrow 4)$ have opposite values.

In the reversible isothermal compressions $4 \rightarrow 5$, there is an entropy variation $Nk(w_1 \ln w_1 + w_2 \ln w_2)$ (cf. Appendix C), *to be attributed to the translation motion only*: $\Delta S_{trans}(4 \rightarrow 5) = Nk(w_1 \ln w_1 + w_2 \ln w_2)$. There is no entropy variation for the system {translation motions, spins} in $5 \rightarrow 6$ (the spins then remain in pure states, and the physical conditions for the molecules K_i don't change), and the same is true in $6 \rightarrow 7$ (during $6 \rightarrow 7$, the molecules $\{K_i, \mathbf{S}_i\}$ are indistinguishable, and there is no change of the total entropy when isothermally bringing together $w_1 N$ molecules initially occupying a volume $w_1 V$ and $w_2 N$ molecules initially occupying a volume $w_2 V$, moreover keeping their total volume equal to V).

To summarize, *from 2 to 7*, the entropy of the whole system {translation motions, spins} displays a variation equal to $Nk(w_1 \ln w_1 + w_2 \ln w_2)$, which is negative, i.e. this entropy decreases. The N "molecules" occupy the same volume V at the same temperature T , both in the initial state 2 and in the final state 7, so the entropy of the translation motions is the same in 2 and in 7, and that decrease is therefore due to the spins only. The entropy variation *per spin* in the whole process $2 \rightarrow 7$ is therefore $k(w_1 \ln w_1 + w_2 \ln w_2)$. Since the final spin state is a pure state, the final spin entropy is 0. Its initial entropy, i.e. that of the initial mixed state was therefore $-k(w_1 \ln w_1 + w_2 \ln w_2)$. For the same reason, in the more general case when $\rho_Q = \sum_n w_n P_{[\varphi_n]}$, the entropy for system \mathbf{S} is

$$S_{VN} = -k \sum_n w_n \ln w_n \quad \text{or} \quad \sigma_{VN} = - \sum_n w_n \ln w_n, \quad (10)$$

which is the von Neumann expression.

In this presentation, we systematically used density operators ρ , which therefore obey $\text{Tr} \rho = 1$. There is of course a difference for the corresponding entropy S_{spins} for the collection of "spins" and that for a single "spin", equal to S_{spins}/N .

Von Neumann's reasoning is therefore quite clear: he postulated that, with any state of a quantum system Σ , described by ρ , one can associate the mean value $S(\rho)$ of a certain function of the Hermitian operator ρ , called the entropy of Σ , and satisfying the constraints of the second principle. Then, to find $S(\rho)$, he accepted the first and second principles of thermodynamics and, *using thermodynamics*, he obtained the VN expression for $S(\rho)$. We gave a detailed treatment of that part of VN's reasoning, as **it is this step which is disputed in** [Shenker 1999; Henderson 2003; Hemmo 2006] (cf. Section 4).

If one associates that part of VN's treatment with the rest of his work upon QSM in [von Neumann 1932, Ch. 5], one can confidently estimate that VN's aim was to check that introducing *his postulates 1 and 2* leads to a coherent building, rather than to get a purely deductive establishment of the principles of thermodynamics, which would mean some circular reasoning.

The constancy of entropy of the whole system {translation motions, spins} during $2 \rightarrow 4$ should not be a surprise. It is true that if, at constant temperature T , two samples of molecules behaving as the model gases of Appendix A, one with $N/2$ molecules of species A in a region with volume $V/2$, and the other with $N/2$ molecules of species B in a distinct region with volume $V/2$, are mixed into a single volume V , then the total entropy is increased by $Nk \ln 2$ (entropy of mixing, cf. Appendix C). But the present separation process $2 \rightarrow 4$ is *not* the inverse of that operation, since before the separation the "molecules" occupy a volume V , and after separation each species still occupies a volume V (and not $V/2$).

VN's procedure for the entropy determinations was called an "arithmetical argument" in [Shenker 1999, end of Sec. 2] and in [Hemmo 2006, e.g. Sec. 2, p. 157].

Our presentation shows that VN's result is in fact a direct consequence of: 1) the existence of an *entropy function* defined A) for the translation motions, for any equilibrium state, B) for the spins, for any (pure or mixed) state described by a density operator ρ , 2) VN's assumption of uncoupling between translation motions and spins and postulate 2. [Shenker 1999] completes VN's succession of stages, in order to get a thermodynamical *cycle*. He then writes that considering that the entropy has the same value in the (thermodynamically identical) initial (1) and final (7) states is an "assumption", which "ignores the heat and work reservoirs". *Speaking of an "assumption" is clearly wrong*, because it does not respect the existence and definition of the entropy function (see e.g. [Callen 1966] and our Appendix C). The reservoirs are helpful in the calculations, and play a role during the transformations (e.g. thermal reservoirs allow to keep the temperature constant, pressure reservoirs allow a reversible behaviour during the compression), but thinking that their presence invalidates the previous entropy variation determinations is confusing between calculations and results of calculations.

3.3 Peres and von Neumann's experiment

The 1995 first edition of Peres's presentation of QM concepts and methods appeared some sixty years after VN's book. [Peres 2002] did use VN's thought experiment, but his aim and approach were quite different from VN's ones in [von Neumann 1932], as may be appreciated through a historical perspective.

With [von Neumann 1932], VN aimed at stabilizing the mathematical foundations of QM and at inserting Gibbs's ideas upon CSM into a quantum context. In Sec. 2 of Ch. 5, VN explicitly indicated that he had to start from the principles of phenomenological thermodynamics. As recalled in our Subsection 3.2, VN inserted \mathbf{S} , the quantum system of interest, into a box K kept at temperature T (and therefore replica \mathbf{S}_i into replica K_i). His two implicit postulates allowed him to apply the principles of **thermodynamics** to $\{K_i, \mathbf{S}_i\}$, a system composed of two species, collections $\{K_i\}$ and $\{\mathbf{S}_i\}$. He could describe the collection of K_i as the "molecules" of an ideal gas, being then able to finally deduce information upon the quantum system \mathbf{S} . Therefore, when VN established his expression for entropy, he used QM mainly for the description of $\{\mathbf{S}_i\}$ (and of \mathbf{S}) with an arbitrary density operator, as declared at the beginning of his Sec. 2 [von Neumann 1932, Ch. 5]: "quantum mechanics plays a role only insofar as our thermodynamical observations relate to such objects whose behavior is regulated by the laws of quantum mechanics".

In 1948, Shannon introduced the concept of information entropy, in a classical context, which then allowed Jaynes to introduce the concept of information into statistical mechanics [Jaynes 1 1957; Jaynes 2 1957; Jaynes 2003]. Jaynes presented statistical mechanics through "a reversal of usual reasoning" [Jaynes 1 1957], **information entropy** being then taken as a starting concept. This approach is e.g. adopted in [Balian 1982]. While this procedure may surprise those used to a traditional exposition (phenomenological thermodynamics, statistical physics, statistical thermodynamics), the beginner should be less reluctant. Such a change, not infrequent in the development of physics, comes with social changes: Clausius defined entropy after the industrial development of steam engines, Gibbs's extension to open systems followed the development of chemistry, with chemical reactions taking place in open subsystems, and Jaynes and his followers start with the concept of information entropy at the Information Age under development.

Peres introduces VN's experiment in Ch. 9 of [Peres 2002], the title of which is unambiguous: "Information and thermodynamics". Peres starts with the information entropy concept. He introduces the entropy concept in a *quantum* context, which

allows him to assess that the (reduced) entropy of a quantum state described by a density operator ρ is $-\text{Tr}(\rho \ln \rho)$ ((9.16) of [Peres 2002]). Peres then refers to [Einstein 1914], cited by VN, and uses VN's thought experiment *and QM* to establish that the quantum entropy defined in this way corresponds to thermodynamic entropy. It should therefore be clear that Peres follows a different approach from VN. Since Peres uses QM before thermodynamics, he needs a quantum treatment of the behaviour of $\{K_i, \mathbf{S}_i\}$, contrary to VN who used thermodynamics first. He then observes that "the hybrid classical-quantum reasoning" found in [Einstein 1914] "is not satisfactory". An exact quantum treatment should *a priori* be difficult for two reasons: 1) getting an exact solution for a quantum mechanical problem is quite exceptional, 2) \mathbf{S}_i is an *arbitrary* quantum system. Because of 1), approximate methods have been developed in QM. So-called semi-classical methods, where \hbar is considered as a parameter and made arbitrarily small, are presently of no interest, because the original paper [Einstein 1914] and [von Neumann 1932] use the fact that the mass of the box K_i is far greater than that of \mathbf{S}_i . This idea is kept in [Peres 2002]. Such a difference between masses is e.g. at the root of the Born-Oppenheimer approximation.

Whereas Peres follows a path quite different from that taken by VN, he shares with him the idea that $-\text{Tr}(\rho \ln \rho)$ is analogous to the entropy of thermodynamics, as shown in the introduction of Section 4. But the important point here is not accumulating approaches favoring this or that opinion. We presently think more important to strictly distinguish between VN's approach and that from Peres, which originates in a viewpoint "from which thermodynamic entropy and information-theory entropy appear as the same *concept*" [Jaynes 1 1957]. For the sake of clarity and in order to limit the size of this discussion, we chose not to examine Peres's approach and will avoid any reference to the use of the information entropy concept in the following Sections.

4 Examining Shenker's and ensuing papers

As recalled in Section 3, in [von Neumann 1932] VN first showed that all pure states have the same entropy, which he decided to take equal to the origin of entropies. He then postulated the existence of quantum semi-permeable walls, and showed that they can separate orthogonal states only. These results, accepted in [Shenker 1999; Henderson 2003; Hemmo 2006], will also be accepted in this Section.

The content of [Shenker 1999] and the argumentation in the ensuing papers [Henderson 2003; Hemmo 2006] led to a rather confusing situation upon the validity of VN's approach. On thorough examination, the existence of a methodological choice in [Shenker 1999] suffices, from a strict logical position, for our evaluation of the relevance of the critics made in that debate upon von Neumann's justification (Subsection 4.1). We however chose to also discuss a few significant elements developed in these three papers, hoping that this would help the interested reader in examining their content (Subsections 4.2 to 4.4).

We first criticize a general claim from Shenker, as it may be influential upon the appreciation of VN's justification. [Shenker 1999 Sec. 1] asserts: " *To appreciate the spirit and problems of von Neumann's attempt it may be useful to compare it with Gibbs's approach.*". Gibbs "drew a very cautious conclusion, namely, the mere existence of an analogy". " *Von Neumann and others claim to have shown*" "that S_{VN} 'is genuine entropy, fully equivalent to that of standard thermodynamics.'⁷ *This claim is by far stronger than Gibbs's*". But in Section 3 we showed that, on the contrary, VN explicitly spoke of an analogy just as Gibbs. The expression "genuine entropy" is not from VN, but from [Peres 2002, p. 270] (cf. also reference 7 in the previous citation from [Shenker 1999]). The question is therefore: what did Peres mean by "genuine

entropy”, and [Peres 2002, p. 274] answered that: “*there should be no doubt that von Neumann’s entropy... is equivalent to the entropy of classical thermodynamics. (This statement must be understood with the same vague meaning as when we say that the quantum notions of energy, momentum, angular momentum, etc., are equivalent to the classical notions bearing the same names.)*”.

The following example illustrates the respective roles of statistical and thermodynamic entropies: critical opalescence (1869, Andrew, in CO_2) is due to large fluctuations in quite specific experimental conditions [Reif 1965]. When VN wrote [von Neumann 1932], the phase transition field was less developed than today, but it was already known that statistical mechanics is able to describe fluctuations, while thermodynamics is not (cf. Section 2). If the system has a volume V and is composed of N microsystems, the physicist formally introduces the “thermodynamic limit”, defined with $V \rightarrow \infty$, $N \rightarrow \infty$, and N/V kept constant (cf. e.g. [Balian 1982]). As a result, in a situation when, e.g., mechanical statistics indicates that a thermodynamic quantity increases with time and that at each instant this quantity fluctuates around its mean value, thermodynamics ignores these fluctuations, by construction knowing only the mean value, and its increase with time. Then, in a situation presenting relative fluctuations roughly equal to $1/\sqrt{N}$, the physicist says that they may practically be neglected. Therefore statistical mechanics may speak of entropy fluctuations around its mean value, while (phenomenological) thermodynamics may not. Less formally, when writing e.g. $PV = nRT$ for an ideal gas, the physicist considers that $N = nN_A$ (N_A : Avogadro number) is finite but macroscopic.

We now examine the above-mentioned critical methodological point and significant elements.

4.1 Shenker’s use of two alternative descriptions

Considering VN’s thought experiment, recalled in our Subsection 3.2, [Shenker 1999] adds stage 1, with conditions identical to those of stage 7: N “molecules” in the same box, with volume V , at T , their “spins” being in the pure state $|\varphi\rangle$. Then, using the notations of Section 3, *and the existence of entropy*:

$$\Delta S(1 \rightarrow 7) = 0, \quad (11)$$

a result valid for any path leading from 1 to 7, reversible or not, since 1 and 7 are identical. But thermodynamics can’t directly give $\Delta S(1 \rightarrow 2)$, for the following reason: while the “molecules” (K_i, \mathbf{S}_i) are not distinguishable at step 1 (all have their spin in state $|\varphi\rangle$), two species do exist at step 2 (the molecules in state $|\varphi_1\rangle$, those in state $|\varphi_2\rangle$). One can however say that:

$$\Delta S(1 \rightarrow 2) + \Delta S(2 \rightarrow 7) = 0. \quad (12)$$

In Section 3, we found that the entropy variation of the whole system {translation motions, spins} from 2 to 7 is equal to $\Delta S(2 \rightarrow 7) = \Delta S_{trans}(4 \rightarrow 5) = Nk(w_1 \ln w_1 + w_2 \ln w_2)$. Therefore:

$$\Delta S(1 \rightarrow 2) = -\Delta S_{trans}(4 \rightarrow 5) = -Nk(w_1 \ln w_1 + w_2 \ln w_2), \quad (13)$$

a result which may be interpreted as follows, using VN’s postulate 2: in the $1 \rightarrow 2$ transformation, S_{trans} does not change (N “molecules” in volume V at T) and the entropy variation $\Delta S(1 \rightarrow 2)$ must therefore be attributed to the “spins”; $\Delta S_{spin}(1 \rightarrow 2) = -Nk(w_1 \ln w_1 + w_2 \ln w_2)$. Since the “spin” entropy is zero for stage 1 (pure state) it is therefore $-Nk(w_1 \ln w_1 + w_2 \ln w_2)$ for the mixed state

of stage 2, i.e. $+Nk \ln 2$ when $w_1 = w_2 = 1/2$ as in [Shenker 1999]. Had Shenker agreed with our presentation of our Section 3, and with this determination and interpretation of $\Delta S(1 \rightarrow 2)$, his 1999 paper would not exist. One has therefore to explain why he does not get VN's result.

VN's cleverness consisted in both applying **thermodynamics to $\{K_i, \mathbf{S}_i\}$** , and taking advantage of: 1) the additivity property for the entropy variations of $\{K_i, \mathbf{S}_i\}$, the sum of the entropy variations of $\{\mathbf{S}_i\}$ (to be found) and of the translation motions $\{K_i\}$, 2) the fact that the spin entropy is the same for all pure states. Careful examination of [Shenker 1999] shows that **Shenker, contrary to VN** (cf. Subsection 3.2), **tries to compare two alternative descriptions of the same system**, the ideal gas, **one with the language of thermodynamics, and one with quantum mechanics**. This is a key point, and there can be no doubt about it, as e.g. he writes [Shenker 1999, Sec. 4]:

1) "*when we move from stage 2 to stage 4, S_{VN} decreases, while from a thermodynamic point of view entropy is conserved*", then adding that "*this impairs Von Neumann's argument*". This is written again at the beginning of his Sec. 5, and is used to show that according to Shenker, "*if S_{VN} is entropy, then perpetual motion machines are possible*",

2) "*Let us focus on the 1 to 4 frame. S_{VN} increases from stage 1 to 2 and then decreases from stage 2 to 4. To deduce that S_{VN} is entropy, in a way analogous to Von Neumann's original arithmetical argument, we must show some correlative changes in the thermodynamic entropy. We must show either that the thermodynamic entropy increases from stage 1 to stage 2, or that it decreases from stage 2 to stage 4*".

But Shenker's comparison can't be made, because at this stage of VN's reasoning it is impossible to determine any entropy variation of a physical system *using quantum mechanics*, since the quantum expression for entropy has still to be found. Trying to carry out this program unavoidably leads either to a circular reasoning, not to be attributed to VN as Shenker does, and/or to inconsistencies. This is illustrated by the following example, concerning the $2 \rightarrow 4$ transformation already considered: this transformation uses semi-permeable walls able to separate two species of "molecules". This means that during the whole $1 \rightarrow 6$ transformation two species of molecules do exist. And in the reversible separation of the "molecules" into two distinct boxes, leading from 2 to 4, the total entropy is unchanged (cf. Section 3.2), which means that an entropy variation of the translation motions is strictly compensated by an opposite entropy variation of the quantum system \mathbf{S} (spin). Shenker, on the contrary, in [Shenker 1999, Sec. 5] writes: "Now we can return to the quantum version of the experiment", and then considers that he can successively apply the principles of thermodynamics and those of QM to the same system, and that the density operator describing this system, " ρ incorporates the effect of the volume available for the system on its quantum state". But at this stage of reasoning it is impossible to determine the entropy variation of the whole system $\{K, \mathbf{S}\}$ using QM (the quantum expression for entropy has still to be found). It is moreover certainly true that "a proper density matrix incorporates all the available information regarding the system" [Shenker 1999, p. 45], but this makes sense only once the physical system has been defined. Shenker has already written that he considers "an ideal gas" of molecules. However, if the density operator ρ did incorporate both the effect of the volume available for the system on its quantum state, and the existence of two species of molecules, it would not have the formal aspect used by Shenker. The quantum entropy variation then considered by Shenker when speaking of S_{VN} is in fact that of another system, namely that of \mathbf{S} , which has no reason to be equal to that of the whole system $\{K, \mathbf{S}\}$.

The two descriptions used by Shenker are moreover incompatible, since Shenker first writes that "*At the initial stage we have an ideal gas in a container, in equilibrium*

with some heat bath”, and then, a few lines further on, adds that ”*The initial state of each molecule is, in terms of a density matrix: $\rho_1 = |a_1\rangle\langle a_1|$. This state is pure*” [Shenker 1999, p. 36]. But it seems irrelevant to a priori exclude the possibility that at thermal equilibrium, at temperature T , the system be described by a density operator $\rho \propto e^{-\mathcal{H}/kT}$, as suggested by CSM, and confirmed by VN’s work and the development of QSM. This last possibility generally corresponds to a statistical mixture, the case of a system with a non-degenerate ground level, in the zero temperature limit, being an exception. It is therefore contradictory to claim that the ”molecules” are both in a pure state and at thermal equilibrium.

Shenker’s error could result from a confusion between VN’s and Peres’s approaches (cf. Subsection 3.3), which could have prevented him from distinguishing between two steps in VN’s reasoning: 1) in his Sec. 2 of Ch. 5, VN applies the principles of thermodynamics to the whole system {translation motions, ”spins”} to get his expression for S_{VN} , which then describes a property of the quantum part \mathbf{S} (”spin”), 2) having found his expression for the entropy of \mathbf{S} , then, in Sec. 3 of Ch. 5 (cf. our Section 3) VN uses that expression and the quantum partition function to associate ”statistical thermodynamic” quantities with a quantum system at thermal equilibrium.

4.2 Shenker’s perpetual motion machines

[Shenker 1999] uses the $2 \rightarrow 4$ transformation to claim that, ”if S_{VN} is entropy, then perpetual motion machines are possible”. That $2 \rightarrow 4$ quasi-static separation process with von Neumann’s device, with two gases and an arbitrary w_1 value, is analyzed in detail in Appendix B, with the use of Fig. 1. In Subsection 4.3, we mention the importance of the chemical potential concept for this analysis, allowing us to prove (cf. Appendix B) that the total force acting on the two jointly moving walls bb and dd is zero, which means that this quasi-static transformation takes place without mechanical work exchange with the outside: Shenker’s machines can’t exist.

In [Shenker 1999], the thermodynamic system is ill-defined: S_{VN} refers to the ”spin” part S of $\{K, \mathbf{S}\}$, whereas the entropy conservation during $2 \rightarrow 4$ is that of $\{K, \mathbf{S}\}$, and Shenker fails to distinguish between them.

4.3 Chemical potentials, measurements, separation

In [Shenker 1999, Sec. 4] Shenker writes that at the end of the $2 \rightarrow 4$ separation process, ”we must know the number of particles on each side in order to obtain equal pressures at the compression step”, and that ”the numbers can be measured by, say, quasi-static weighing”. Thinking that these measurements are necessary implies that the concept of chemical potential introduced in [Gibbs 1875; Gibbs 1902] and its present consequences are ignored, which means treating thermodynamical subsystems systematically as closed systems, even when they are open (sub)systems. This is clearly a misuse of thermodynamics. In fact, in that $2 \rightarrow 4$ quasi-static process, since gas 1 can be permanently exchanged between regions 1 and 1-2, and gas 2 between 2 and 1-2, the chemical potential for the first gas permanently has the same value in regions 1 and 1-2, and the same is true for the chemical potential of gas 2 between 2 and 1-2. As a result (Appendix B), pressure in region 1 keeps equal to the initial partial pressure of gas 1, and pressure in region 2 keeps equal to the initial partial pressure of gas 2, and each one keeps equal to the corresponding partial pressure in region 1-2.

[Shenker 1999] stimulated a reply [Henderson 2003], in which Henderson observed that ”it is important to consider not only the internal, or spin, degrees of freedom of

the particle, but also its spatial degrees of freedom” and that the spatial (i.e. translational) degrees of freedom are thermalized, at temperature T , in agreement with VN. Henderson judiciously stressed that [Shenker 1999] had considered the spin part only. Unfortunately, having identified the existence of the two uncoupled parts (“translation” and “spin”), Henderson then was not able to keep her distance from [Shenker 1999]. She first reproduced the major error consisting in trying to successively apply thermodynamics and quantum (statistical) mechanics to the same physical reality, explicitly writing “We will compare what we expect thermodynamically to what we calculate using the Von Neumann entropy”. This led her to start considerations upon the quantum state of the spin part \mathbf{S} and upon the question of quantum measurements, which, we think, even increased the confusion.

More explicitly, Henderson agrees with everybody that, at the beginning of the $2 \rightarrow 4$ separation process, and in the specific case $w_1 = w_2 = 1/2$ chosen by Shenker, the spin part is in the mixed state $\rho = I/2$ (I being the identity operator within the two-dimensional spin space). Then, considering the end of this separation, step 4, she notices that “Shenker claims that the state of the system at this stage is pure”, and then tries to show that, on the contrary, the spin part remains in the mixed state. In her lengthy argument, Henderson starts by considering the $1 \rightarrow 2$ transformation, having claimed that: “Von Neumann’s argument runs as follows. In the initial state, we have a gas of particles each in the pure state $|+\rangle = 1/\sqrt{2}(|0\rangle + |1\rangle)$, occupying a box of volume V . A measurement is then made in the $(|0\rangle, |1\rangle)$ basis, giving an equally weighted mixture of particles in states $|0\rangle$ and $|1\rangle$ ”, i.e. step 2 [Henderson 2003, p. 292]. In fact, contrary to what Henderson writes paraphrasing [Shenker 1999], step 1 and the $1 \rightarrow 2$ transformation were not proposed by VN but by Shenker (cf. our Subsection 4.1). Since the entropies of \mathbf{S} and of $\{K, \mathbf{S}\}$ at step 2 do not depend upon the way the given quantum mixture was obtained, then if one starts from step 2, as VN did, the part of the discussion of [Henderson 2003] pertaining to her measurement act leading to 2 becomes useless and can be ignored. We therefore concentrate upon the $2 \rightarrow 4$ separation process, and the quantum description of \mathbf{S} and/or $\{K, \mathbf{S}\}$, supposing it presents some interest.

Henderson denotes the density operator for the spatial (i.e. translational) degrees of freedom at thermal equilibrium (given by the canonical law) as ρ_s , and writes that any molecule, *after the separation*, is in the state:

$$\rho = \frac{1}{2}(|0\rangle\langle 0| + |1\rangle\langle 1|) \otimes \rho_s \quad (\text{Henderson}). \quad (14)$$

This expression is wrong, because ρ_s , given by the canonical law, is a function of the Hamiltonian. This Hamiltonian is defined only in the volume occupied by the “spatial” motion of the molecule. Henderson writes it as a common factor for $|1\rangle$ and $|0\rangle$, which means that molecules with $|1\rangle$ state and those with $|0\rangle$ state are in the same spatial region. This implies that the nominally semi-permeable walls were in fact unable to bring molecules with spin $|0\rangle$ into region 1 and those with spin $|1\rangle$ into region 2, contrary to the assumption of a separation process, recalled in [Henderson 2003, p. 292]. *In fact, at stage 4 one has molecules in region 1, with spin in the pure state $|0\rangle$, and molecules in region 2, with spin in the pure state $|1\rangle$.*

4.4 Justification, or verification?

Momentarily staying with [Henderson 2003], we come to its claim that: “the Von Neumann entropy of ρ_s is $S(\rho_s) = c(T) + \log V$, where c is a constant depending on temperature”. It is true that e.g. from the model gas of our Appendix A and (26) one

can easily deduce that the entropy of a fixed quantity of gas (closed system) at T in a volume V obeys a relation of the form $S(T, V) = a(T) + b \ln V$, but this $S(T, V)$ expression for *thermodynamic* entropy should not be confused with the expression $S(\rho_s)$ for the VN entropy. One may try to consider that the expression in [Henderson 2003] comes from QSM results for thermal equilibrium. But such results have yet to be set up at this stage of VN's reasoning, since VN established his expression $S = -k \text{Tr} \rho \ln \rho$ in Sec. 2 of Ch. 5, and only then, in the second part of Sec. 3, did he establish the canonical law, using his expression for entropy. What Henderson tries to do here is then **not a justification** (of VN's formula for S), **but a verification** (of the coherence of quantum statistics with thermodynamics).

The abstract of [Hemmo 2006], a reply to [Henderson 2003], unambiguously stresses that its aim is still to analyze VN's thought experiment. Its introduction states that it argues that "Von Neumann's argument does not establish the desired conceptual linkage between $\text{Tr} \rho \ln \rho$ and thermodynamic entropy $(1/T) \int p dV$ ". This claim introduces a possible new misunderstanding: choosing a thermodynamical system with equilibrium states defined in the energy representation [Callen 1966] by a function $U(S, V, n)$, then, when that system is *closed*, the thermodynamical identity reduces to $dU = T dS - P dV$. And in a reversible infinitesimal transformation, since the work of the pressure forces acting on that system is $DW_r = -P dV$, the thermal exchange with the external world verifies $DQ_r = T dS$, i.e. the Clausius definition of entropy. If moreover **the transformation is isothermal ($dT = 0$) and the system is an ideal gas**, then its internal energy does not change, and $dS = P dV/T$, therefore in a finite reversible transformation:

$$\Delta S = \frac{1}{T} \int_{rev} P dV \quad \text{rev: reversible path.} \quad (15)$$

This expression for an entropy *variation of a closed system* is therefore quite specific. Moreover, there is strictly no reason why it should always be equal to the entropy of another system, with quantum behaviour. What VN established, with both the thermodynamical system he had defined and what can be called his trick (this word for the transformations he imagined), is that *the sum* of the entropy of his quantum system of interest and of an entropy variation of this form was zero, which gave him a *general* expression for the entropy of the quantum system. So the two quantities are not equal but turn out to be opposite (cf. Subsection 3.2). One should then rather understand that [Hemmo 2006] starts by accepting VN's expression for the entropy of a quantum system, S_{VN} , and then tries to compare the result given by VN's expression with that from thermodynamics, adding stage 1 to VN's thought experiment and successively considering three compositions of the gas: "a single particle", "finitely many particles" and "the limit of finitely many particles". As [Henderson 2003], this program of [Hemmo 2006] is therefore quite distinct from VN's work recalled in Subsection 3.2. Whereas [Henderson 2003] was a verification, [Hemmo 2006] claims to establish that entropy variations calculated with S_{VN} fail to equal the corresponding variations using thermodynamics. This would make sense only if, for both calculations (thermodynamics, S_{VN} with QM), the same well-defined thermodynamical system were used for the same transformation.

We first focus on that part of [Hemmo 2006] treating macroscopic systems ("finitely many particles" and "the limit of finitely many particles"). In [Hemmo 2006], in the determination of entropy variations with thermodynamics, open subsystems are treated as closed subsystems, as in [Shenker 1999] (cf. Subsection 4.3), which leads Hemmo and Shenker to consider that "in order to perform a quasi-static compression a measurement of the location (L or R) of the particles is necessary". As a consequence, the determination of the thermodynamic entropy variations in [Hemmo 2006] is wrong. Examining the determination of the expression for S_{VN} then becomes

superfluous, and we limit ourselves to a few comments. This determination of S_{VN} would anyway be a hard task, as it is somewhat similar to that met when building QSM. Since e.g. it aims at a comparison with thermodynamical results obtained under definite experimental conditions (isothermal transformations of an ideal gas), adequate assumptions should then be made, e.g. thermal equilibrium and constant temperature for the translational motion.

We now come to the case of one particle. In [von Neumann 1932, Ch. 5], once he had established his S_{VN} expression (Sec. 2), von Neumann verified that S_{VN} does not decrease in a measurement process (first part of Sec. 3), and found the QSM analogs of (7) and (8) (second part of Sec. 3). Then, von Neumann did consider a gas with one particle for a discussion of macroscopic measurements (Sec. 4), another subject than the one treated in our paper. In the case of a gas with one particle, Hemmo and Shenker [Hemmo 2006] notice that applying the laws of thermodynamics to a single particle is "problematic", but add that they "do not address this issue", which neither eliminates nor solves the problem. Clearly, with a few particles or a single one, the intensive quantities, pressure, temperature and chemical potential loose their meaning [see e.g. Feshbach 1987]. Then, should a disagreement appear in the comparison between the results from VN's expression and those from thermodynamics used in these conditions (which VN avoided when establishing his formula for S_{VN}), it would then be careful not to incriminate the S_{VN} expression. If, following [Hemmo 2006], one decides to forget the difficulty, momentarily assuming that the laws of thermodynamics valid for one mole are also valid for one molecule (the extensive quantities being just divided by N_A), which allows one to keep expression (15), a difficulty soon appears: the results of Subsection 4.3 and Appendix B are then still valid, and the pressure for a given gas is the same in both regions during the separation process. It is therefore impossible then to say that at the end of the separation (step 4) the single molecule is in region 1 *or* in region 2, contrary to what is done in the analysis given in [Hemmo 2006, Subsec. 3.1]. This contradiction invalidates the conclusions of that analysis.

We end up with a comment about (in)distinguishability. Today, indistinguishability of identical particles may be viewed as an experimental reality, responsible for exchange, a purely quantum phenomenon e.g. giving rise to the ferromagnetism of iron. The identical atoms or molecules of a gas are indistinguishable. Thermodynamics is so built that it does respect the indistinguishability of identical particles. In [Shenker 1999, p. 37], the molecules of a gas are implicitly assumed to be distinguishable, an idea explicitly kept in [Henderson 2003, p. 293; Hemmo 2006, p. 165]. **In a context of verification** of the coherence of QSM with thermodynamics, what are the consequences of erroneously treating these molecules as distinguishable? Calling $|0\rangle$ and $|1\rangle$ two orthonormal states for the "spin" of a "molecule", then a molecule with spin state $|0\rangle$ and one with state $|1\rangle$ are distinguishable and may be separated, but e.g. all the "molecules" *found in region 1* at the end of the separation have the same spin state, *and are then indistinguishable*. And denoting the partition function of a single "molecule" as Z_0 , the partition function for N_1 identical independent "molecules" in this region is not $Z = Z_0^{N_1}$ (distinguishable particles), but $Z \simeq Z_0^{N_1}/N_1!$ (indistinguishable particles in classical regime) [Reif 1965]. If one uses $Z = Z_0^{N_1}$, then, in the entropy expression calculated with (8), a term $-k \ln N_1! \simeq -k N_1 \ln N_1$ will be missing, whereas, in a transformation of this closed system of N_1 molecules, that term will not be missing (it should be present both in the initial and final entropy expressions).

5 Landau and the von Neumann entropy

[Shenker 1999] states: "to the best of my knowledge, no other justification" (than the one in [von Neumann 1932] examined by Shenker) "has so far been given to the opinion that S_{VN} is entropy", an idea reproduced in [Hemmo 2006]. In already cited [Feynman 1972], devoted to applications of QSM, the concept of entropy is introduced through the VN expression, at thermal equilibrium, without any comment about the choice for this definition of entropy. Another justification can however be found, in Vol. 5 (Statistical Mechanics) of the Course of Theoretical Physics by Landau and Lifshitz, the second edition of which [Landau 1958] was earlier than 1962 Landau's accident. Landau and von Neumann had independently introduced the density operator ρ into QM in 1927. Landau had worked with Bohr in Copenhagen around 1929, and his ideas upon QM were close to Bohr's approach. He asserts from the very beginning of Vol. 3 (non relativistic QM) of the Course [Landau 1967], that QM is not logically closed, as it contains classical mechanics as a limiting case, but needs classical mechanics in order to get founded. Landau's exposition of statistical mechanics reflects that position. He starts with quantum statistical mechanics, introducing the statistical entropy through a quantum version of the Boltzmann postulate $S_B = k \ln W$ which, in the classical limit, has to agree with it. He then derives the Liouville-Von Neumann relation (cf. Section 1), the quantum analog of Liouville's theorem of classical mechanics, and finally establishes the relation $\sigma = -\text{Tr} \rho \ln \rho$. In his approach, nowhere has thermodynamics been solicited. The content of the principles of thermodynamics, thermodynamic quantities such as pressure, and general relations existing between them, are presented in later chapters, from the general principles of statistical mechanics (cf. e.g. in Sec. 13: $DQ_{rev} = TdS$, i.e. Clausius relation). Landau's approach uses the following path: Boltzmann postulate \rightarrow VN expression \rightarrow thermodynamic quantities \rightarrow (quantum) Gibbs law. Following Landau, [Kittel 1969] also introduces thermodynamics through statistical mechanics only, without resorting to phenomenological thermodynamics.

6 Discussion

On the whole, one should clearly distinguish between the following three *expressions* for entropy: 1) the one used by (phenomenological) thermodynamics, defined for equilibrium states, and which takes the form $S(T, V, n)$ for the simplest systems of Section 2, T being an independent variable (cf. Appendix A), 2) the expression of the VN entropy, $S_{VN} = -k\text{Tr}(\rho \ln \rho)$, defined for any state, mixed or pure, of any quantum system, 3) the value of the VN entropy when a quantum macroscopic system is at thermal equilibrium. The VN expression therefore operates as a bridge between the *thermodynamic entropy* and the *equilibrium QSM entropy*, i.e. the entropy calculated for quantum macroscopic systems at thermal equilibrium using e.g. (the quantum version of) (8). It is now possible to complete the beginning of Subsection 4.4, suggested by [Henderson 2003]: it is relevant to try and compare $S(T, V, n)$ from thermodynamics (macroscopic system, equilibrium), not with the general expression $S_{VN} = -k\text{Tr}(\rho \ln \rho)$, but with the results from equilibrium QSM, derived e.g. from (the quantum version of) (8). The comparison obviously must use the same system, respectively viewed as a thermodynamical system and modeled at the microscopic level. The two expressions should be compatible, but not identical (the quantum expression, and only it, contains microscopic quantities). This behaviour, reflecting the distinct roles of (phenomenological) thermodynamics and QSM, can be illustrated e.g. by the Sackur-Tetrode relation (e.g. cf. [Kittel 1969, p. 167]), expressing the quantum entropy of an ideal monoatomic gas. This relation, which contains the quantum

volume $V_Q = (2\pi\hbar^2/mkT)^{3/2}$ (m : mass of an atom, \hbar : reduced Planck constant), is compatible with but cannot be obtained using thermodynamics. This comparison is meaningful in both the VN and the Landau approaches, in a context of *verification* of the coherence of QSM with thermodynamics (cf. Subsection 4.4). Historically, while the form of the Sackur-Tetrode relation had been discovered experimentally, this relation was firmly established only after the creation of QSM. It could be submitted to experimental tests, which have been successful (Clusius, 1936, cf. [Kittel 1969, p. 169]), a fact historically strongly in favour of the validity of QSM, and implicitly of the correctness of von Neumann's ideas upon (quantum) entropy.

The above short incursion into the development of QSM after [von Neumann 1932] both shows a key position of VN's expression in statistical mechanics and the possibility of establishing it without any use of VN's approach. The complexity of VN's argumentation and the existence of Landau's and Jaynes's approaches may explain why most physicists ignore VN's justification, which then mainly keeps a historical interest in the context of a presentation of QSM, while it obviously occupies a central place in the debate discussed in Section 4.

7 Conclusion

By referring to their own writings, we could show that successively Gibbs, von Neumann and recently Peres spoke of an *analogy* between thermodynamic entropy and the entropy introduced in classical and quantum statistical mechanics. Gibbs's and VN's texts, written before the 1948 Shannon paper initiating the development of Information Theory, made no reference to the information concept, but started from the concept of thermodynamic entropy. On the contrary, Peres's recent book starts from the concept of information entropy, following Jaynes's ideas. For that reason, for the sake of clarity and of an economy of space, we did not discuss Peres's approach, although it both uses VN's thought experiment and agrees with VN's conclusions. In the recent debate about the link between thermodynamic and von Neumann entropies discussed in Section 4, the existence of quantum semi-permeable walls, and VN's result that all pure quantum states have the same entropy, have been accepted, and so we did in Section 4. We showed that, once the existence of an entropy $S(\rho)$ associated with each quantum state, described by ρ , is postulated (von Neumann's postulate 1), then, taking the entropy of pure states as the origin of entropy, one gets the expression S_{VN} proposed by von Neumann for $S(\rho)$. This expression is the quantum analog of the definition of entropy introduced by Gibbs in a classical context, ρ being the probability density in phase space Γ . Then using his expression for S_{VN} , VN, in a quantum context, established relations (7) and (8) previously obtained by Gibbs in classical physics. This last result, which allowed von Neumann to say that $-k\text{Tr}(\rho \ln \rho)$ is the quantum statistical entropy, had not been previously examined or even mentioned in the debate of Section 4. Moreover, we especially identified two facts which deeply affected this debate: a misuse of thermodynamics (treatment of open subsystems as closed subsystems) and a misunderstanding of VN's approach (alternative use of thermodynamics and QM in the debate, instead of VN's sole use of thermodynamics).

VN's expression $\sigma_{VN} = -\text{Tr}(\rho \ln \rho)$ was introduced without any use of the justification given by VN in [von Neumann 1932], successively by Landau, Kittel, and with another approach by those following Jaynes, e.g. Balian and Peres. This change reflects the fact that physics is not only a mental/experimental construction, but also a social activity, a reality which more deeply explains why today classical statistical mechanics is seen as a province of quantum statistical mechanics.

A Ideal gas with T-independent C_V : U and μ

[Callen 1966, p. 52] derives the expression of the chemical potential μ for an ideal monoatomic gas ($\gamma = 5/3$) from the Gibbs-Duhem equation:

$$d\left(\frac{\mu}{T}\right) = \frac{U}{n}d\left(\frac{1}{T}\right) + \frac{V}{n}d\left(\frac{P}{T}\right), \quad (16)$$

a consequence of the Euler equation $U = TS - PV + \mu n$. The same approach may be used for the chemical potential of any ideal gas with temperature-independent C_V , and leads to (4). It makes use of the following equations of state:

$$\frac{1}{T} = \frac{R}{\gamma - 1} \frac{n}{U} \quad \text{and} \quad \frac{P}{T} = R \frac{n}{V}. \quad (17)$$

Use of relation $U = (3/2)nRT$ in [Callen 1966], when deriving the expressions for μ and S , may suggest that this justification can't avoid calling upon statistical mechanics. We presently aim at showing that one may establish (4), which especially holds when $\gamma = 5/3$, *without any reference to statistical mechanics*. Starting from the fundamental relation $S(U, V, n)$ and (3), one first notices that $1/T = (\partial S/\partial U)_{V,n}$ is a function of (U, V, n) , and therefore U may be seen as a function $U(T, V, n)$. A gas is said to obey the first Joule law if, for it, $U(T, V, n)$ is V -independent: $(\partial U/\partial V)_{T,n} \equiv 0$. Now introducing $U(S, V, n)$, the fundamental relation in the internal energy representation, one rewrites (3) as

$$dU = TdS - PdV + \mu dn, \quad (18)$$

which shows that $P = -(\partial U/\partial V)_{S,n}$ is a function $P(S, V, n)$. V and U can therefore be seen as functions of S, P, n . One then introduces the relation $H = U + PV$, defining the enthalpy function $H(S, P, n)$, and its differential:

$$dH = TdS + VdP + \mu dn. \quad (19)$$

$T = (\partial H/\partial S)_{P,n}$ is a function of (S, P, n) . S and H may therefore be seen as functions of T, P, n . A gas is said to obey the second Joule law if its enthalpy $H(T, P, n)$ is P -independent: $(\partial H/\partial P)_{T,n} \equiv 0$. A gas is said to be ideal if it both obeys the first and the second Joule laws. This is one of the possible definitions, chosen here as in [Bruhat 1962]. The definitions of H and of an ideal gas require that:

$$PV = H(T, n) - U(T, n). \quad (20)$$

By considering a transformation of n moles of an ideal gas from (P, V, T) to $(P + dP, V + dV, T + dT)$, one can show that PV is proportional to T [Bruhat 1962]. The proportionality constant can't be obtained by thermodynamics, but from experience: $PV = nRT$, with $R = 8.314 \text{ J.K}^{-1}\text{mole}^{-1}$. From general thermodynamic relations and the definition of an ideal gas, it follows that C_P does not depend upon P but only on T and n , that C_V does not depend upon V but only on T and n , and that $C_P - C_V = nR$ (Meyer relation), therefore $C_V = nR/[\gamma(T) - 1]$. Thermodynamics can't give the $\gamma(T)$ law. This information must be obtained from experiments. The behaviour of monoatomic or diatomic gases in definite (P, T) domains allows us to introduce the model of **an ideal gas with C_V (and therefore C_P and γ) being temperature-independent** (VN assumes it in his note 191), and with $U(T = 0) = 0$. For such a gas, $U = nRT/(\gamma - 1)$, since $(\partial U/\partial V)_{T,n} = 0$ for an ideal gas. We thus obtained both equations of state (17) which, inserted into (16), lead to (4).

B Chemical potentials and separation process

We examine the $2 \rightarrow 4$ separation process, keeping the framework of thermodynamics, with *two distinct gases* 1 and 2 obeying the model of Appendix A (e.g. argon and neon, with $\gamma = 5/3$). Insofar as the existence of quantum semi-permeable walls has been accepted in this debate, the results to follow are valid for the systems examined in this paper. Initially, $w_1 n = n_{1t}$ (t : total) moles of gas 1 and $w_2 n = (1 - w_1)n = n_{2t}$ moles of gas 2 occupy the same region, with volume V . After separation, each gas occupies a volume V . Figure 1 represents an intermediate state in that $2 \rightarrow 4$ separation with VN's device (Section 3). bb and dd walls are quasi-statically moved to the left, and jointly (their distance is kept constant). Wall (2,5) is fixed and semi-permeable, being transparent to gas 1, but opaque to gas 2. Wall dd is transparent to gas 2 but opaque to gas 1. Wall bb is opaque to both gases. We denote the chemical potential of gas 1 (resp. 2) in region i as $\mu_1(i)$ (resp. $\mu_2(i)$). Since regions 1 and 1-2 may exchange gas 1, $\mu_1(1) = \mu_1(1-2)$. Since regions 2 and 1-2 may exchange gas 2, $\mu_2(2) = \mu_2(1-2)$.

In stage 2, partial pressures P_{10} for gas 1 and P_{20} for gas 2 verify:

$$P_{10}V = n_{1t}RT \quad ; \quad P_{20}V = n_{2t}RT \quad (21)$$

In an intermediate state when region 1, containing n_1 moles of gas 1, has a volume V_1 , then region 2, containing n_2 moles of gas 2, has a volume V_2 . Since the distance between pistons bb and dd is kept constant, then $V_1 = V_2 = v$. Pressures P_1 in region 1 and P_2 in region 2 then verify:

$$P_1 v = n_1 RT \quad \text{and} \quad P_2 v = n_2 RT. \quad (22)$$

The chemical potential μ for a given gas verifies (cf. (4) and Appendix A):

$$\frac{\mu}{T} = R \ln \frac{U^{\frac{1}{1-\gamma}} V^{-1} n^{\frac{\gamma}{\gamma-1}}}{(U^{\frac{1}{1-\gamma}} V^{-1} n^{\frac{\gamma}{\gamma-1}})_0} + \left(\frac{\mu}{T}\right)_0. \quad (23)$$

The temperature is kept constant, $U = nRT/(\gamma - 1)$, and $\mu_1(1) = \mu_1(1-2)$; therefore n/V has the same value for gas 1 in regions 1-2 and 1; the same is true for n/V of gas 2 in regions 1-2 and 2, i.e.:

$$\frac{n_1}{v} = \frac{n_{1t} - n_1}{V_{12}} = \frac{n_{1t}}{V} \quad \text{and} \quad \frac{n_2}{v} = \frac{n_{2t} - n_2}{V_{12}} = \frac{n_{2t}}{V}. \quad (24)$$

The concentration of the first gas in region 1 is therefore equal to its concentration before the beginning of separation, and the same is true for gas 2 in region 2. Moreover, from these relations:

$$P_1 = P_{10} \quad \text{and} \quad P_2 = P_{20}, \quad (25)$$

i.e. pressure in region 1 is permanently equal to the partial pressure of gas 1 before the beginning of separation, and the same is true for pressure in region 2 and the partial pressure of gas 2. There is truly a pressure P_1 acting upon wall bb, and a pressure $(P_{10} + P_{20}) - P_2 = P_1$ acting upon wall dd, which moves jointly with wall bb. However, the total force acting upon {bb,dd} is zero. Thermodynamically, the total internal energy U of the gases is the same at stages 2 and 4 (ideal gases, same temperature). During $2 \rightarrow 4$, $\Delta U = Q_r + W_r$, and since $\Delta U = 0$ and $W_r = 0$, then $Q_r = T\Delta S$ is zero: during the $2 \rightarrow 4$ transformation, the entropy of the gases is conserved (in [von Neumann 1932, note 199] VN justified the constancy of entropy in the separation process by referring to Planck's treatise). Coming now to $\{K, \mathbf{S}\}$: the entropy of the system $\{K, \mathbf{S}\}$ does not change during the $2 \rightarrow 4$ reversible transformation.

C Some entropy balances

Knowing the three equations of state $1/T$, P/T , μ/T (as functions of U, V, n) for the model gas of Appendix A (cf. (17) and (4)), and using Euler equation and a reference state (index 0), one gets its fundamental relation $S(U, V, n)$:

$$S = n \left[R \ln \frac{U^{\frac{1}{\gamma-1}} V n^{-\frac{\gamma}{\gamma-1}}}{(U^{\frac{1}{\gamma-1}} V n^{-\frac{\gamma}{\gamma-1}})_0} + \frac{S_0}{n_0} \right]. \quad (26)$$

Use of $S(U, V, n)$ gives an easy access to entropy variations, making clear the assumptions made. For instance, in the $2 \rightarrow 4$ separation process examined in Appendix B, the entropy S of the system formed by the two gases 1 and 2 is the sum of the entropies S_1 and S_2 of each gas, at stage 2 (the two gases are uncoupled, a fact implicit when speaking of partial pressures in Appendix B), and at stage 4 (they are in distinct regions). Therefore the entropy variation ΔS of that system between 2 and 4 is:

$$\Delta S = (\Delta S)_1 + (\Delta S)_2. \quad (27)$$

The $w_1 n$ moles of gas 1 keep their volume, and their internal energy (same temperature, ideal gases). Therefore $(\Delta S)_1 = 0$. The same is true for gas 2, and the total entropy is therefore constant as already found in Appendix B. This result **implicitly uses the chemical potential concept** (through the derivation of $S(U, V, n)$ from the Euler equation).

Now, if the $w_1 n$ moles of gas 1 and $w_2 n$ moles of gas 2 initially occupying distinct regions with respective volumes $w_1 V$ and $w_2 V$ are mixed into the same volume V , there is a total entropy increase (entropy of mixing) equal to $-nR(w_1 \ln w_1 + w_2 \ln w_2)$ (cf. (27) and (26)).

In Sections 3 and 4, we distinguished the "molecules" through their quantum states (part \mathbf{S} of $\{K, \mathbf{S}\}$). *We now suppose that the n moles of gas following the model of Appendix A are all identical* (e.g. gas 1). It would be wrong to keep the reasoning of the first situation in this appendix and to conclude that the total entropy is still conserved, because *separation with semi-permeable walls is now meaningless*. One can however imagine that *the initial volume is expanded from $V_i = V$ to $V_f = 2V$* , the other conditions being unchanged (temperature T). Then introducing a wall separating the volume $2V$ into two identical regions, each with volume V , would not change the total entropy. In the expansion, there is an entropy increase equal to:

$$\Delta S = nR \ln \frac{V_f}{V_i} = nR \ln 2. \quad (28)$$

One should distinguish between the isothermal separation of two species of molecules initially in the same volume V , leading to a volume V for each species (total entropy is then conserved) and the isothermal expansion from V to $2V$ of a single species (total entropy then increases).

The results in this appendix are also valid for the (K_i, \mathbf{S}_i) "molecules", because there is no coupling between the elements of a Gibbs ensemble, and moreover VN assumed C_V to be temperature-independent.

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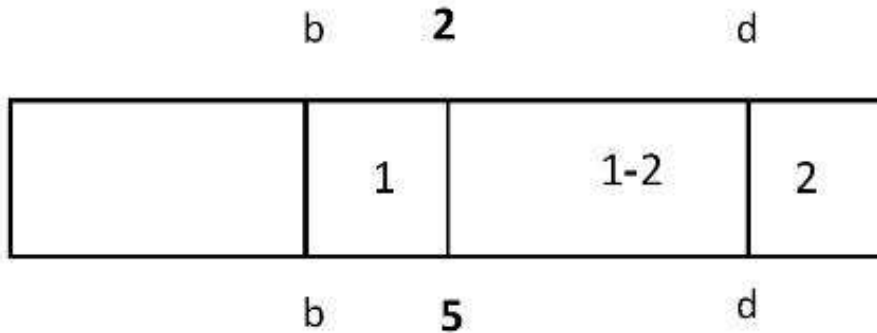


Fig. 1. Regions, species and walls in separation process.