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On the mechanical foundations of thermodynamics: The generalized Helmholtz theorem

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Abstract

An elegant but seldom appreciated effort to provide a mechanical model of equilibrium thermodynamics dates back to the Helmholtz theorem (HT). According to this theorem, the thermodynamic relations hold mechanically (without probabilistic assumptions) in the case of one-dimensional *monocyclic* systems. Thanks to a discrete picture of the phase space, Boltzmann was able to apply the HT to multi-dimensional *ergodic* systems, suggesting that the thermodynamic relations we observe in macroscopic systems at equilibrium are a direct consequence of the microscopic laws of dynamics alone. Here I review Boltzmann's argument and show that, using the language of the modern ergodic theory, it can be safely re-expressed on a continuum phase space as a generalized Helmholtz theorem (GHT), which can be readily proved. Along the way the agreement between the Helmholtz–Boltzmann theory and that of P. Hertz (based on *adiabatic invariance*) is revealed. Both theories, in fact, lead to define the entropy as the logarithm of the phase-space volume enclosed by the constant energy hypersurface (*volume entropy*).

Keywords: Heat theorem; Equipartition; Ergodic theory; Micro-canonical; Metric indecomposability; Adiabatic invariance; Volume entropy.

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1. Introduction

The object of statistical mechanics is that of deriving macroscopic laws from the underlying microscopic laws, thus its aim may be thought as that of providing a theoretical model which could possibly explain how macroscopic behaviour emerges from the microscopic dynamics. Since the birth of statistical mechanics a debate is going on regarding the conditions that are relevant for such emergence. On one hand, many authors emphasize the role the very large number of degrees of freedom may play, in other words, at some point, they invoke the law of large numbers and the thermodynamic limit (TD limit): their approach might be labelled as "statistical". On the other hand, many consider general dynamical properties such as, for instance, ergodicity, mixing or sensitivity to initial conditions, as fundamental ingredients: their viewpoint might be seen as mainly "mechanical".

Even though here the "mechanical" viewpoint has been adopted, it is plausible to admit that neither a purely mechanical, nor a purely statistical theory would probably be enough to account for the whole wide variety of macro-phenomena observed in Nature. Nevertheless, as we shall see, it seems reasonable that, as far as we are concerned only with equilibrium thermodynamics, and in particular with the *heat theorem*, the laws of Hamiltonian mechanics alone, in the special case of ergodic systems, may provide a satisfactory explanation.

This viewpoint has been recently suggested by Gallavotti (1999) in his "*Short treatise of Statistical Mechanics*", where the problem of the emergence of equilibrium thermodynamics from the underlying micro-physics is addressed by going back in time to the early Boltzmann and Helmholtz' works about monocyclic systems (Boltzmann, 1884, Helmholtz, 1884a,b). According to Gallavotti the programme of Boltzmann was that of proving the validity of the *heat theorem*:

$$\mathrm{d}S = \frac{\mathrm{d}E + P\,\mathrm{d}V}{T} \tag{1}$$

in great generality, from the one-dimensional system to the 10^{23}-dimensional one, relying only on mechanical quantities which were to be named with suitable thermodynamic names. The first half of the programme, namely, the one-dimensional case, had been successfully treated by Helmholtz, and nowadays is known (unfortunately just to a minority of physicists) as the *Helmholtz theorem*.[1] With the introduction of the *ergodic hypothesis* Boltzmann paved the way towards the study of the general multi-dimensional case. Gallavotti discusses this issue in a clear way and shows that a generalization is possible which provides a mechanical, size independent, foundation of equilibrium thermodynamics, based on Boltzmann's discrete picture of the phase space (Gallavotti, 1999, Section 9.1).

It is important to stress that there exist alternative mechanical approaches in the literature. One of the most popular (especially within the German school, see e.g.

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[1] Not to be confused with the better known HT of classical electrodynamics.

(Münster, 1969; Becker, 1969)) can be traced back to Hertz (1910), who bases statistical mechanics on the principle of *adiabatic invariance*, namely

$$\Delta S = 0, \tag{2}$$

where the symbol ΔA denotes the change of the quantity A due to an adiabatic transformation, and S is the entropy of the system. The adoption of this principle eventually brought Hertz to the proposal, still not widely recognized unfortunately, of the "volume entropy" (instead of the usual "surface entropy") as the only form of entropy consistent with both *adiabatic invariance* and the *equipartition theorem* (a modern exposition of this approach recently appeared in Berdichevsky (1997)).

The volume entropy may play an important role also in more modern mechanical approaches such as, for example, the dynamical Fokker–Planck equation approach proposed by Bianucci, Mannella, West, and Grigolini (1995). These authors focused on the linear response of a particle (the system of interest) coupled to a Fermi–Pasta–Ulam chain with quartic interactions (the booster), and put forward a mechanical expression of the system's temperature which was found to be consistent, apart from $O(1/N)$ corrections (interpreted as "dynamical" corrections), with the adoption of the surface entropy (namely with Boltzmann's counting principle) for the unperturbed booster. Recent developments of their work (Adib, 2004) show, with the support of numerical simulations, that a correction is unneeded provided that the surface entropy is replaced by the volume entropy.

In order to prevent possible misunderstandings of this work, it is necessary to emphasize that, with respect to thermodynamics, this paper refers only to *equilibrium* states and *quasi-static* transformations where the system remains arbitrarily close to equilibrium. Having reduced the scope of the study to such cases, questions regarding irreversible processes, out of equilibrium phenomena and the law of entropy increase are far out of the scope of the present work. To be more precise, the second law of thermodynamics is commonly understood as being composed of two parts which conventionally will be referred here as "part A" and "part B". "Part A" states that there exists an integrating factor $(1/T)$ such that $\delta Q/T$ is an exact differential (dS), whereas "part B" states that the change in entropy in a thermally isolated system which undergoes a transformation between two equilibrium states is non-negative ($\Delta S \geqslant 0$). "Part A" expresses the exactness of the heat differential (the heat theorem), whose mechanical foundations are the object of this paper. "Part B", a principle of entropy increase, is not addressed here.

The paper is organized as follows. Section 2 is a review of surface and volume entropies: I briefly discuss their properties, mutual relationships, and their role in statistical mechanics. Section 3 deals with the HT and its extensions to multi-dimensional systems, developing Boltzmann's argument leads to a straightforward and easy to prove generalization, which employs the modern notion of ergodicity and the volume entropy. Section 4 is devoted to some concluding remarks. An appendix includes a brief discussion of how the theorem relates to the micro-canonical ensemble.

2. Surface and volume entropy

Usually two entropic functions are discussed in textbooks (see for instance (Huang, 1963)) for thermally isolated systems: the *surface entropy*:

$$S_\Omega(E, V) = \log \Omega(E, V), \tag{3}$$

where

$$\Omega(E, V) = \int \frac{d\mathbf{\Gamma}}{h^{3N}} \delta[E - H(\mathbf{z}, V)] \tag{4}$$

and the *volume*[2] *entropy*

$$S_\Phi(E, V) = \log \Phi(E, V), \tag{5}$$

where

$$\Phi(E, V) = \int \frac{d\mathbf{\Gamma}}{h^{3N}} \theta[E - H(\mathbf{z}, V)]. \tag{6}$$

The symbol δ represents the one-dimensional Dirac's delta-function, θ represents the Heavyside step-function; $\mathbf{z} = (\mathbf{p}, \mathbf{q})$ is a point in the $6N$-dimensional phase space $\mathbf{\Gamma}$. The Hamiltonian is $H(\mathbf{z}, V) = K(\mathbf{p}) + \varphi(\mathbf{q}, V)$. The potential φ includes both particle–particle and container–particle interactions, the container "coordinate" (i.e., its volume V) is treated as an "external" parameter. h is a constant with the dimensions of an action introduced as a convention.[3] The quantity $\Omega(E, V)$ represents the volume of the infinitesimally thin shell of constant energy E in the phase space $\mathbf{\Gamma}$ (surface integral), while $\Phi(E, V)$ represents the volume of the region enclosed by the hyper-surface of constant energy E (volume integral). Following Khinchin (1949, see p. 32), we will assume the energy to have a lower bound, which for convenience will be set equal to zero. It is important to notice that, with a further assumption of "smoothness" of the hyper-surfaces of constant energy, the following relation holds:

$$\Omega = \frac{\partial}{\partial E} \Phi. \tag{7}$$

Also, in most cases, for very large N,

$$\Omega \sim \Phi. \tag{8}$$

Both entropies are known to provide the correct thermodynamics (Huang, 1963). Historically S_Ω had been favored by theoreticians, nevertheless in practical calculations S_Φ is usually preferred for it is easier to evaluate. For the purposes of this paper, it is worth discussing some properties of these two entropies in more detail. This discussion helps confronting them, and introducing the HT.

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[2] Sometimes "bulk".

[3] I do not include the celebrated Gibbs correction factor $1/N!$ for it is not essential in this context.

2.1. Properties of the surface entropy

From a formal point of view, the surface entropy plays an important role in statistical mechanics for its close connection with the micro-canonical distribution. Defining the micro-canonical distribution as following:

$$\rho_\mu(\mathbf{z}, E, V)\frac{\mathrm{d}\mathbf{\Gamma}}{h^{3N}} = \frac{\delta[E - H(\mathbf{z}, V)]}{\mathit{normalization}}\frac{\mathrm{d}\mathbf{\Gamma}}{h^{3N}}, \tag{9}$$

the normalization factor would be given exactly by the surface integral Ω. This is why often Ω is referred to as the partition function of the micro-canonical ensemble. Thanks to Eq. (9) the surface integral enters explicitly in the expression of the micro-canonical average of a physical quantity on the surface of constant energy i.e.,

$$\langle f \rangle_\mu \equiv \frac{\int (\mathrm{d}\mathbf{\Gamma}/h^{3N}) f(\mathbf{z}) \delta[E - H(\mathbf{z}, V)]}{\Omega(E, V)}. \tag{10}$$

From a mathematical perspective Ω also plays the role of the Jacobian of the change of variables $\mathbf{z} \to E$, which makes easy the evaluation of average values of observables of the type $f(E(\mathbf{z}))$:

$$\frac{\mathrm{d}\mathbf{\Gamma}}{h^{3N}} = \Omega(E, V)\,\mathrm{d}E. \tag{11}$$

Because of this relation Ω is also important in the passage from classical to quantum statistical mechanics, in fact Ω counts the "density of states at a given energy" (degeneracy).

From a physical point of view, the surface entropy is interesting as, in the limit of very large N, it approaches Boltzmann's counting entropy ($S_W = \log W$) of the given equilibrium state. Nevertheless the counting entropy is at the same time more and less general than the surface entropy. More general in the fact that it applies both to equilibrium and out of equilibrium states, whereas the surface entropy is restricted to equilibrium; less general in the fact that, unlike the surface entropy, it applies only to ideal gases (Uffink, 2004).

2.2. Properties of the volume entropy

After the seminal work of Hertz (1910), it is a known fact that the volume integral Φ is an adiabatic invariant, and it has been recognized that this very fact plays a significant role in the mechanical foundations of thermodynamics. To show this, let us first provide a definition of adiabatic invariant. Let $H(\mathbf{z}, V)$ be the Hamiltonian of a system which depends on an external parameter whose value changes in time according to some law: $V = V(t)$, and let τ be the characteristic time of variation of V. Through the dependence on V the Hamiltonian depends explicitly on time, hence the energy is not conserved (work is performed on the system by changing the parameter V from outside), accordingly the energy will change in time with some temporal law $E(t)$.

Definition 1. A function $I(E, V)$ is named an *adiabatic invariant* if, in the limit of very slow variation of $V(t)$, namely as $\tau \to \infty$, $I(E(t), V(t)) \to$ *const*.

Note that the qualifier "adiabatic" in the context of Hamiltonian mechanics has a quite different meaning than in thermodynamics, where it is used as synonymous of "thermally isolated". For example, with reference to Definition 1, in mechanics an adiabatic transformations is a very slow transformation during which the adiabatic invariant remains constant. This meaning of "adiabatic" matches with that of the thermodynamic expression "quasi-static", rather than "thermally isolated".[4] In other words, in studying thermodynamic systems as many-body mechanical systems interacting with an externally driven field of forces, it is quite reasonable to model quasi-static transformations as adiabatic processes (Toda, Kubo, & Saitô, 1983, see Section 2.3.2). It is natural, then, to model the quantities which remain constant along quasi-static transformations as mechanical adiabatic invariants.

Now consider "part B" of the second law of thermodynamics (see Section 1), $\Delta S \geqslant 0$, and recall that the "=" sign refers to quasi-static transformations: it is a basic fact of thermodynamics that along a quasi-static transformation between two equilibrium states of a thermally isolated system, the entropy (which, for the exactness of the heat differential, is a function of E and V) is a constant. In modelling this fact from a mechanical perspective, then, as Hertz has done, it is natural to require the mechanical expression of entropy to be an adiabatic invariant. Hertz had also shown that, for any number of degrees of freedom, the volume integral (Eq. (6)) is an adiabatic invariant *provided that the system be ergodic*.[5] This means that the candidate mechanical expression of entropy should be a function of Φ: $S = f(\Phi)$. If one takes a look at the equipartition theorem (which is valid independent of the dimensionality of the system as well), the reason why Hertz was led to choose the entropic function to be of the form of a logarithmic function becomes clear. Note in fact that the equipartition theorem (Khinchin, 1949, p. 104), reads

$$\langle K \rangle_\mu = \frac{1}{2}\left\langle \mathbf{p} \cdot \frac{\partial H}{\partial \mathbf{p}} \right\rangle_\mu = \frac{3N}{2}\frac{\Phi(E, V)}{\Omega(E, V)} \tag{12}$$

or equivalently (use Eq. (7))

$$\left(\frac{2\langle K \rangle_\mu}{3N}\right)^{-1} = \frac{\partial}{\partial E} \log \Phi(E, V). \tag{13}$$

From this perspective, the equipartition theorem expresses a very general dynamical–geometrical property of Hamiltonian systems which, as soon as we agree to name the quantity $(2\langle K \rangle_\mu / 3N)$ as "temperature", reads as the fundamental thermodynamic relation $T^{-1} = \partial S / \partial E$. As a natural consequence, we have to agree

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[4] This is also reflected by the fact that a quasi-static process is understood as a so slow process that it can be thought of as a virtual sequence of equilibrium states, as much as the adiabatic process is so slow that the motion can be thought of as driven by a sequence of "frozen" (i.e. time independent) Hamiltonians (Jarzynsky, 1992).

[5] This is why Φ is sometimes referred to, in literature, as *the ergodic adiabatic invariant* (Brown, Ott, & Gregobi, 1987; Jarzynsky, 1992).

to name the quantity $\log \Phi(E, V)$ as “entropy”. In sum, *for ergodic systems*, the volume entropy has two remarkably good properties: it is an adiabatic invariant and it is consistent with the equipartition theorem.

The approach of Hertz has been recently re-expressed by Berdichevsky (1997) adopting a modern viewpoint. In particular, Berdichevsky showed that under the hypothesis of *metric indecomposability* (see Definition 2 below) the volume entropy is an adiabatic invariant and that any other adiabatic invariant is necessarily a function of Φ only. This latter statement leaves no room for alternative definitions of entropy within the approach of Hertz and it is in contrast with the claim by Toda et al. (1983), that the surface integral is also an adiabatic invariant. Indeed, that the surface integral is not in general an adiabatic invariant can be seen by considering as a counter example the 1D harmonic oscillator (which is trivially ergodic) with slowly varying frequency ω. The ergodic adiabatic invariant in this case would be the action variable $\Phi = E/\omega$ (Landau & Lifshitz, 1960), therefore the surface integral $\Omega = (\partial/\partial E)\Phi = 1/\omega$, would be trivially non-constant. In the thermodynamic limit, anyway, on the basis of Eq. (8), it is expected that the surface entropy approaches adiabatic invariance.

3. Helmholtz’ theorem and generalization

In this section I will review the HT concerning one-dimensional systems and I will follow the lines of Boltzmann–Gallavotti (Gallavotti (1999), Section 9.1) to show how it can be employed in the general multi-dimensional case. By proceeding along the same lines, I will show that, in the multi-dimensional case, the Helmholtz entropy is nothing but the volume entropy of Hertz. This will provide the input for the formulation of a general version of the theorem, expressed in the modern language of ergodic theory, which can be readily proved.

3.1. Helmholtz’ theorem

As mentioned before, the aim of this theorem is that of providing a mechanical model of thermodynamics based on one-dimensional systems. Boltzmann intended to generalize such theory to multi-dimensional systems in order to unify micro- and macro-physics in one consistent picture using ergodicity as the key tool.

The theorem applies to one-dimensional conservative systems in a confined potential where there is only one periodic trajectory per energy level, i.e., it applies to what Helmholtz called one-dimensional *monocyclic* systems (Gallavotti (1999), p. 38). To cite some examples, the harmonic oscillator and a particle in a box are one-dimensional monocyclic systems, a particle inside a double well potential is not because under a certain energy value there are two distinct trajectories per energy level. Roughly speaking the theorem applies to one-dimensional Hamiltonian systems with a U-shaped potential. Let us recall the theorem without proof:

Theorem 1 (*Helmholtz*). *Let $H(p, q; V) = p^2/2m + \varphi(q; V)$ be the Hamiltonian of a one-dimensional* monocyclic *system. Let a* state *be characterized by the set of quantities*:

$$\begin{aligned} &E = \textit{total energy} = K + \varphi, \\ &T = \textit{twice the time average of the kinetic energy} = 2\langle K \rangle_t, \\ &V = \textit{the external parameter}, \\ &P = \textit{minus the time average of } \frac{\partial \varphi}{\partial V} = \left\langle -\frac{\partial \varphi}{\partial V} \right\rangle_t, \end{aligned} \tag{14}$$

then the differential

$$\frac{\mathrm{d}E + P\mathrm{d}V}{T} \tag{15}$$

is exact,[6] *and $S_{\mathrm{H}}(E, V)$*,[7] *defined as*

$$S_{\mathrm{H}}(E, V) = \log 2 \int_{x_-(E,V)}^{x_+(E,V)} \frac{\mathrm{d}x}{h} \sqrt{2m(E - \varphi(x, V))} \tag{16}$$

is the generating function, *i.e.*,

$$\mathrm{d}S_{\mathrm{H}} = \frac{\mathrm{d}E + P\mathrm{d}V}{T}, \tag{17}$$

where the symbols $x_\pm(E, V)$ denote the turning points of the trajectory, *i.e.*, *the roots of the equation $E - \varphi(x, V) = 0$.*

As the reader can easily note, this theorem says that there is a class of mechanical systems which provide a model of thermodynamic behaviour. Once we attach the thermodynamic names of temperature and entropy to T and S_{H}, respectively,[8] the thesis reads exactly as "part A" of the second law of thermodynamics (see Section 1). For such systems, the heat theorem holds as a consequence of Hamiltonian mechanics alone.

3.2. Generalized Helmholtz' theorem

3.2.1. Discrete version

According to Gallavotti's reconstruction of Boltzmann's ergodic hypothesis (Gallavotti (1999), see Section 9.1 and Appendix 9.A.3), thanks to a discrete picture of phase space, Boltzmann saw how the HT could be applied to multi-dimensional systems. The argument of Gallavotti goes as follows: imagine that we divide the phase space in cells of same size and then consider the time evolution of the system as a map which transforms a cell into another, that is a *permutation* of the phase space cells on the hyper-surface of constant energy. This permutation is in general

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[6] This is often referred to as the *heat theorem* (Gallavotti (1999)).

[7] The subscript H stands for Helmholtz.

[8] P can be proved to be the average momentum transfer to the confining walls per unit time, therefore it has its own mechanical interpretation of pressure.

decomposable in sub-permutations, or *cycles*, involving only a fraction of the total cells. This happens, for instance, when extra integrals of motion are present besides the energy: cells with different values of these integrals do not transform into each other but just among themselves defining the aforementioned cycles. The discrete ergodic hypothesis of Boltzmann–Gallavotti (the reader may find a detailed account in (Gallavotti (1999), Section 1.3)) is that there is only *one* cycle per energy level, i.e., that the discrete trajectory visits *all* the phase space points (cells) with a given energy. A system satisfying such a hypothesis will be referred to as a discrete ergodic system in this paper. For such systems, the motion can be followed along a curvilinear abscissa running along the trajectory itself, reducing the dynamics of the multi-dimensional system to that of a one-dimensional *monocyclic* system to which the HT can be applied. More explicitly, let us discretize the phase space in hyper-cubic cells of volume $h^{3N} = (\Delta q \Delta p)^{3N}$. Consider the trajectory in the discrete configuration space as an ordered sequence of cells labelled by a counter j, and let $\ell = j\Delta q$ be the distance travelled by the representative point (ℓ is, so to speak, a "discrete curvilinear abscissa"). Let us now define the sequence

$$\ell \to \mathbf{q}(\ell) \tag{18}$$

which assigns the cell centred at $\mathbf{q}$ to the travelled distance ℓ. The representative point spends different times in different cells. Denoting the sojourn time in the jth cell with the symbol Δt_j, allows to define the velocity $\dot{\ell} \doteq \Delta q/\Delta t_j$ associated with ℓ. For such a discrete system then, the conservation of energy would read

$$\frac{1}{2m} p_\ell^2 + \varphi(\mathbf{q}(\ell), V) = E, \tag{19}$$

where $p_\ell = m\dot{\ell}$. If the original system is a discrete ergodic system, the above equation describes the motion of a one-dimensional system living in the phase space (ℓ, p_ℓ), where it draws *one* closed trajectory for each energy specification: namely it is a one-dimensional *monocyclic* system. Therefore, the HT applies suggesting that

> "Thermodynamic relations are [...] very general and simple consequences of the structure of the equations of motion: they hold for small and large systems, from one degree of freedom [...] to 10^{23} degrees of freedom [...]" (Gallavotti (1999), p. 266)

which is a remarkable result indeed because it implies that an expression for the entropy in terms of the Hamiltonian must exist for any system size. Such a mechanical expression of entropy, namely the multi-dimensional counterpart of the Helmholtz entropy (Eq. (16)), is missing in the Boltzmann–Gallavotti argument, but it can be found by continuing their argument. Let us express the Helmholtz entropy associated with a discrete ergodic system, we have[9]

$$S_{\mathrm{H}}(E, V) = \log \int_0^{\mathcal{N}\Delta q} \frac{\mathrm{d}\ell}{h} \sqrt{2m[E - \varphi(\mathbf{q}(\ell), V)]}. \tag{20}$$

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[9] Here the symbol $\int_0^{\mathcal{N}\Delta q} \mathrm{d}\ell f(\ell)$ is a convenient notation for $\Delta q \sum_{j=0}^{\mathcal{N}} f(j\Delta q)$.

where $\mathcal{N}\Delta q$ is the total distance travelled in one cycle. Note that the right hand side of Eq. (20) depends explicitly on the sequence $\mathbf{q}(\ell)$ which afterwards can be computed only after integrating the complete set of Hamilton's equation, which, as N gets large, becomes a practically impossible task. In order to evaluate S_{H} we will use the following "trick". As noticed before, the dynamics of the system can be alternatively depicted either in the $6N$-dimensional phase space Γ or in the two-dimensional phase space (ℓ, p_ℓ). If we express the kinetic energy in both representations, we get

$$\frac{1}{2m}p_\ell^2 = \frac{1}{2m}\sum_{i=1}^{3N} p_i^2. \tag{21}$$

By taking the time average and then applying the equipartition theorem (Eq. (13)) to both sides of Eq. (21) we get (remembering that on the left we are dealing with a one-dimensional system, whose curve of constant energy "encloses" an area A, and on the right we have a $3N$-dimensional system whose hyper-surface of constant energy encloses a volume Φ):

$$3N\frac{\partial}{\partial E}\log A(E,V) = \frac{\partial}{\partial E}\log \Phi(E,V). \tag{22}$$

Then, by integration (with the condition $A|_{E=0} = \Phi|_{E=0}$) follows the simple formula:

$$\log \Phi = 3N \log A. \tag{23}$$

Note that the area under the trajectory in the phase space of a one-dimensional system can be expressed as the action integral (Landau & Lifshitz, 1960):

$$A = \oint \frac{p_\ell \, \mathrm{d}\ell}{h}. \tag{24}$$

On the other hand $p_\ell = \sqrt{2m[E - \varphi(\mathbf{q}(\ell), V)]}$, hence $\log A$ is the Helmholtz entropy, therefore

$$S_\Phi(E,V) = 3NS_{\mathrm{H}}(E,V). \tag{25}$$

This result is surprising as it reveals that (apart from the multiplicative factor) the Helmholtz entropy of a discrete ergodic systems is nothing but the volume entropy, therefore the volume entropy generates the heat differential of discrete ergodic systems. The result is important both from a theoretical viewpoint as it constitutes a link between the mechanical approach of Helmholtz–Boltzmann to that of Hertz, and from a practical viewpoint because it allows to calculate S_{H} without solving Hamilton's equations.

It is important to stress that Eqs. (19)–(25) are all discrete equations, and as such, hold to good approximation only for fine enough discretizations.

3.2.2. Continuum version

In order to pass to the continuum let us focus on Eq. (25) and note that, though S_{H} requires a discrete space to be well-defined (how could otherwise the one-dimensional phase trajectory fill the $6N-1$-dimensional hyper-surface?), the volume entropy appearing on the left-hand side of Eq. (25) can be safely defined on the continuum (which is indeed the usual case). This suggests (a) to consider the volume entropy as a good continuum counterpart of the Helmholtz entropy of a discrete ergodic system, and (b) that a general formulation of the HT may be attempted which does not rely on a discrete structure. Proceeding in this direction would require in particular the employment of a notion of ergodicity based on the continuum instead of the Boltzmann–Gallavotti discrete one.

The notion of *metric indecomposability* seems to be very well suited for this purpose. Let us recall that in the modern ergodic theory (Khinchin, 1949),

Definition 2. A portion Π of the phase space is called metrically indecomposable, if:

- Π is invariant under the Liouville evolution induced by H, and
- Π cannot be represented in the form $\Pi = \Pi_1 + \Pi_2$, where Π_1 and Π_2 are invariant disjoint subsets of positive measure.

Two remarks are needed at this point: (1) metric indecomposability extends the notion of one-dimensional monocyclicity to any dimension, (2) metric indecomposability extends the Boltzmann–Gallavotti discrete notion of ergodicity to the continuum. The first remark follows from the fact that in the case of one-dimensional monocyclic systems, any hyper-surface of constant energy in the phase space (they are indeed curves) is metrically indecomposable. This is a consequence of the fact that each trajectory draws *one* complete constant energy curve. For example, for a non-monocyclic system like a particle inside a double well potential, all the curves with lower energy than a certain value are in fact decomposable in two sub-curves drawn by distinct trajectories with same energy. The second remark follows as one notes that the Boltzmann–Gallavotti ergodicity expresses the impossibility of decomposing the time-evolution permutation into sub-permutations as much as metric indecomposability expresses the impossibility of decomposing the Liouville flow into disjoint sub-flows: they express the same concept onto a discrete and a continuum space respectively.

Two analogous remarks apply to the volume entropy: ($1'$) the volume entropy is the generalization of the Helmholtz entropy (Eq. (16)) to any dimension, ($2'$) the volume entropy is the generalization of discrete ergodic systems' entropy (Eq. (20)) to the continuum. Remark ($1'$) follows by direct check that the volume entropy in 1D is equal to the Helmholtz entropy, by integration over dp one gets

$$\int \frac{\mathrm{d}x\,\mathrm{d}p}{h}\theta\left(E-\frac{p^2}{2m}-\varphi(x,V)\right) = 2\int_{x_-(E,V)}^{x_+(E,V)} \frac{\mathrm{d}x}{h}\sqrt{2m(E-\varphi(x,V))}. \tag{26}$$

Remark ($2'$) has been already discussed (see point (a) above).

It is not a surprise, then, that volume entropy and metric indecomposability can be employed to formulate a generalized Helmholtz theorem (GHT), which on one hand extends the HT to any dimension, and on the other extends the Boltzmann–Gallavotti ideas to the continuum:

Theorem 2 (*Helmholtz, generalized*). *Let* $H(\mathbf{p},\mathbf{q};V)$ *be the Hamiltonian of a mechanical system with* $3N$ *degrees of freedom. Let any hyper-surfaces of constant energy in the* $6N$*-dimensional phase space* $\mathbf{\Gamma}$ *be metrically indecomposable. Let a* state *be characterized by the set of quantities*:

$$\begin{aligned}
&E = \textit{total energy} = K + \varphi,\\
&T = \textit{twice the time average of the kinetic energy per degree of freedom}\\
&\quad = (2\langle K\rangle_t/3N),\\
&V = \textit{the external field},\\
&P = \textit{time average of } -\partial\varphi/\partial V = -\langle\partial\varphi/\partial V\rangle_t,
\end{aligned} \tag{27}$$

then, the differential

$$\frac{\mathrm{d}E + P\,\mathrm{d}V}{T} \tag{28}$$

is exact, and the volume entropy,

$$S_\Phi(E,V) = \log \Phi(E,V), \tag{29}$$

is the generating function, i.e.

$$\mathrm{d}S_\Phi = \frac{\mathrm{d}E + P\,\mathrm{d}V}{T}. \tag{30}$$

Proof. The differential of $S_\Phi(E,V)$ is:

$$\mathrm{d}S_\Phi = \frac{\partial S_\Phi}{\partial E}\,\mathrm{d}E + \frac{\partial S_\Phi}{\partial V}\,\mathrm{d}V, \tag{31}$$

using the definition of Eqs. (5) and (6)

$$\begin{aligned}
\frac{\partial S_\Phi}{\partial E} &= \frac{1}{\Phi}\left(\frac{\partial}{\partial E}\int \frac{\mathrm{d}\mathbf{\Gamma}}{h^{3N}}\theta[E - H(\mathbf{z},V)]\right)\\
&= \frac{1}{\Phi}\left(\int \frac{\mathrm{d}\mathbf{\Gamma}}{h^{3N}}\delta[E - H(\mathbf{z},V)]\right)\\
&= \frac{\Omega}{\Phi},
\end{aligned} \tag{32}$$

$$\begin{aligned}
\frac{\partial S_\Phi}{\partial V} &= \frac{1}{\Phi}\left(\frac{\partial}{\partial V}\int \mathrm{d}\mathbf{\Gamma}\theta[E - H(\mathbf{z},V)]\right)\\
&= -\frac{1}{\Phi}\left(\int \mathrm{d}\mathbf{\Gamma}\delta[E - H(\mathbf{z},V)]\frac{\partial}{\partial V}H(\mathbf{z},V)\right)\\
&= -\frac{\Omega}{\Phi}\left\langle\frac{\partial H}{\partial V}\right\rangle_\mu,
\end{aligned} \tag{33}$$

where use is made of Eqs. (3) and (10) and of the relation $\frac{\mathrm{d}}{\mathrm{d}E}\theta = \delta$. For Birkhoff's ergodic theorem (Khinchin, 1949), metric indecomposability of the hyper-surface of constant energy implies that the time average of any summable phase function *f* over (almost) any trajectory belonging to the hyper-surface, does not depend on the trajectory itself and is equal to its phase average i.e.,[10]

$$\langle f \rangle_t = \langle f \rangle_\mu. \tag{34}$$

Thanks to Eq. (34), we can interchangeably use the subscript μ or t for the averages. This implies

$$-\left\langle \frac{\partial H}{\partial V} \right\rangle_\mu = -\left\langle \frac{\partial H}{\partial V} \right\rangle_t = P. \tag{35}$$

Thanks to the equipartition theorem (Eq. (13)), we also get

$$\frac{\Phi}{\Omega} = \frac{2\langle K \rangle_\mu}{3N} = \frac{2\langle K \rangle_t}{3N} = T. \tag{36}$$

Combining all these together the thesis straightforwardly follows:

$$\mathrm{d}S_\Phi = \frac{1}{T}\,\mathrm{d}E + \frac{P}{T}\,\mathrm{d}V. \tag{37}$$

4. Concluding remarks

It is worth to notice that the GHT can be easily extended to any number of external "coordinates" $\boldsymbol{\lambda} = (\lambda_1, \lambda_2, \ldots, \lambda_r)$. By defining the conjugate "forces" with:

$$P_j = -\left\langle \frac{\partial H(\mathbf{z}, \boldsymbol{\lambda})}{\partial \lambda_j} \right\rangle_t, \quad j = 1 \ldots r, \tag{38}$$

the theorem would read

$$\mathrm{d}S_\Phi = \frac{\mathrm{d}E + \sum P_j\,\mathrm{d}\lambda_j}{T}. \tag{39}$$

An important fact is that, adopting the Helmholtz–Boltzmann viewpoint, we can derive *equilibrium* thermodynamics from mechanics without incurring in the "methodological paradox", mentioned by Khinchin (1949, p. 41), of neglecting inter-molecular interactions. Indeed, we are forced to include the interaction term in the Hamiltonian, otherwise the system would fail to be ergodic and Boltzmann's ideas (either in their original or modern form) would not apply. This is because ergodicity means a situation of complete *non-integrability*,[11] which ultimately stems from the impossibility of reducing the system (through a canonical transformation) to a

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[10] For clarity, systems with metrically indecomposable hyper-surfaces will be referred to, in the text, as Birkhoff ergodic systems.

[11] The presence of integrals of motion besides the energy, in fact, would decompose the surface of constant energy.

simpler one with no interactions. In this sense, the "disaster" of non-integrability surprisingly turns out, indeed, to be the savior: in the very case when the possibility of a microscopic description is completely out of our reach, the thermodynamic one is made available.

Remarkably, the GHT tells that the heat theorem holds mechanically for Birkhoff ergodic systems *of any size*, which, therefore, provide a good mechanical model of thermodynamics. Taking Gallavotti's reconstruction as starting point, the Helmholtz–Boltzmann theory has been re-expressed within the frame of the modern ergodic theory and has been found to agree with Berdichevsky (1997) reconstruction of Hertz' theory: both deal with Birkhoff ergodic systems[12] and through different paths (in one case the starting point is the requirement that the entropy generate the heat differential, in the other case the entropy is required to be an adiabatic invariant) reach the same mechanical expression of entropy, hence the same thermodynamics. Adopting Hertz' approach the heat theorem would follow as a corollary, adopting that of Helmholtz–Boltzmann adiabatic invariance would follow. Both theories, remarkably, are based on microscopic dynamics and the ergodic hypothesis only: never statistical notions (like probability distributions or the law of large numbers) are invoked, in this sense the GHT is a theorem of ergodic Hamiltonian mechanics which has a straightforward thermodynamic interpretation.

As stressed in the Introduction, the present paper has dealt only with *equilibrium* thermodynamics and in particular with "part A" of the second law, hence no conclusion can be drawn about the law of entropy increase on the basis of the GHT. Nevertheless, since the two parts of the second law are necessarily interconnected, the latter might prove useful in addressing the law of entropy increase from a novel viewpoint, which will have a mechanical basis, but this time, in principle, will benefit from statistics as well. Further studies will be devoted to develop such viewpoint.

By re-expressing Gallavotti's reconstruction of Boltzmann's ideas in the language of the modern ergodic theory, and noting that they agree with those of P. Hertz and followers, I hope this work will help stimulate a broader interest in this mechanical approach to thermodynamics which, despite of its formal elegance, simplicity and richness, seems to have escaped the attention of a large part of the modern scientific community.

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[12] Recall that the volume entropy is the *ergodic adiabatic invariant*.

Appendix A. Generalized Helmholtz theorem and the micro-canonical orthode

Though the mechanical viewpoint has been adopted in this paper, some results found here may be employed in the theory of statistical ensembles as well, this is because, thanks to the ergodic hypothesis, micro-canonical and time averages coincide. This appendix is devoted to a quick indication of how the GHT relates to the problem of *orthodicity* of statistical ensembles as raised by Boltzmann himself (Boltzmann, 1884). A detailed discussion of this topic, including the interpretation of stationary distributions as thermodynamic equilibrium states, is out of the scope of this work.[13] Here, the focus is only on the fact that *formally* the condition of orthodicity of the micro-canonical ensemble coincides with the thesis of the GHT (Eq. (28)). In general, if κ is a distribution belonging to a statistical ensemble ε,[14] and if a state is defined by the quantities

$$E_\kappa = \langle H \rangle_\kappa \quad T_\kappa = \frac{2\langle K \rangle_\kappa}{3N} \quad V_\kappa = \langle V \rangle_\kappa \quad P_\kappa = -\left\langle \frac{\partial \varphi}{\partial V} \right\rangle_\kappa, \tag{A.1}$$

where $\langle \cdot \rangle_\kappa$ denotes κ average

Definition A.1. The ensemble ε is named an *orthode* if an infinitesimal change of κ within ε[15] would cause infinitesimal changes in the state in such a way that the differential:

$$\frac{\mathrm{d}E_\kappa + P_\kappa \,\mathrm{d}V_\kappa}{T_\kappa} \tag{A.2}$$

is exact, at least in the TD limit ($N \to \infty$, and N/V, $U/V \to const$). If the differential (A.2) is exact for any number of degrees of freedom ε is named an *exact orthode*.

If we apply this definition to the micro-canonical ensemble, the requirement of orthodicity would read

$$\left\langle \frac{2K}{3N} \right\rangle_\mu^{-1} \left(\mathrm{d}E - \left\langle \frac{\partial H}{\partial V} \right\rangle_\mu \mathrm{d}V \right) = \textit{exact differential},$$

which, thanks to the equivalence of micro-canonical and time averages, formally coincides with the thesis of the GHT (28). Boltzmann (1884) claimed that both canonical and micro-canonical ensembles are exact orthodes. A proof that the latter is an orthode appears in (Gallavotti, 1999, see Eq. (2.2.12) and Section 2.6) where the surface entropy differential has been found to be equal to the heat differential up to

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[13] The reader may find a detailed discussion in (Gallavotti (1999), Section 1.9).

[14] For example the distribution of Eq. (9) belongs to the micro-canonical ensemble.

[15] This is performed by changing the parameters upon which κ depends: for example E and V in the case of micro-canonical ensemble, T and V in the case of canonical ensemble.

$0(1/N)$ corrections, i.e.

$$\mathrm{d}S_\Omega = \left\langle \frac{2K}{3N} \right\rangle_\mu^{-1} \left(\mathrm{d}E - \left\langle \frac{\partial H}{\partial V} \right\rangle_\mu \mathrm{d}V \right) + 0\left(\frac{1}{N}\right).$$

On the contrary, as from the proof of the GHT, the differential of the volume entropy is *exactly* equal to the heat differential, i.e.,

$$\mathrm{d}S_\Phi = \left\langle \frac{2K}{3N} \right\rangle_\mu^{-1} \left(\mathrm{d}E - \left\langle \frac{\partial H}{\partial V} \right\rangle_\mu \mathrm{d}V \right),$$

which confirms Boltzmann's claim. As a consequence, the volume entropy is the *exact* entropy associated with the micro-canonical orthode.

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