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Chapter 5

Thermodynamics' Microscopic Connotations

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Additional information is available at the end of the chapter

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1. Introduction

Thermodynamics is the science of energy conversion. It involves heat and other forms of energy, mechanical one being the foremost one. Potential energy is the capacity of doing work because of the position of something. Kinetic energy is due to movement, depending upon mass and speed. Since all objects have structure, they possess some internal energy that holds such structure together, a kind of strain energy. As for work, there are to kinds of it: internal and external. The later is work done on "something". The former is work effected within something, being a capacity. Heat is another king of energy, the leit-motif of thermodynamics. Thermodynamics studies and interrelates the macroscopic variables, such as temperature, volume, and pressure that are employed to describe thermal systems and concerns itself with phenomena that can be experimentally reproducible.

In thermodynamics one is usually interested in special system's states called equilibrium ones. Such states are steady ones reached after a system has stabilized itself to such an extent that it no longer keeps changing with the passage of time, as far as its macroscopic variables are concerned. From a thermodynamics point of view a system is defined by its being prepared in a certain, specific way. The system will always reach, eventually, a unique state of thermodynamic equilibrium, univocally determined by the preparation-manner. Empiric reproducibility is a fundamental requirement for physics in general an thermodynamics in particular. The main source of the strength, or robustness, of thermodynamics, lies on the fact does it deals only with phenomena that are experimentally reproducible.

Historically, thermodynamics developed out the need for increasing the efficiency of early steam engines, particularly through the work of the French physicist Nicolas Sadi-Carnot (1824) who believed that a heat engine's efficiency was to play an important role in helping France win the Napoleonic Wars. Scottish physicist Lord Kelvin was the first to formulate a succint definition of thermodynamics in 1854: "Thermodynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency". Chemical thermodynamics studies the role of entropy in the process of chemical reactions and provides the main body of knowledge of the field. Since Boltzmann in the 1870's,

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statistical thermodynamics, or statistical mechanics, that are microscopic theories, began to explain macroscopic thermodynamics via statistical predictions on the collective motion of atoms.

1.1. Thermodynamics' laws

The laws of physics are established scientific regularities regarded as universal and invariable facts of the universe. A "law" differs from hypotheses, theories, postulates, principles, etc., in that it constitutes an analytic statement. A theory starts from a set of axioms from which all laws and phenomena should arise via adequate mathematical treatment. The principles of thermodynamics, often called "its laws", count themselves amongst the most fundamental regularities of Nature [1]. These laws define fundamental physical quantities, such as temperature, energy, and entropy, to describe thermodynamic systems and they account for the transfer of energy as heat and work in thermodynamic processes. An empirically reproducible distinction between heat and work constitutes the "hard-core" of thermodynamics. For processes in which this distinction cannot be made, thermodynamics remains silent. One speaks of four thermodynamics' laws:

- The zeroth law of thermodynamics allows for the assignment of a unique temperature to systems that are in thermal equilibrium with each other.
- The first law postulates the existence of a quantity called the internal energy of a system and shows how it is related to the distinction between energy transfer as work and energy transfer as heat. The internal energy is conserved but work and heat are not defined as separately conserved quantities. Alternatively, one can reformulate the first law as stating that perpetual motion machines of the first kind can not exist.
- The second law of thermodynamics expresses the existence of a quantity called the entropy S and states that for an isolated macroscopic system S never decreases, or, alternatively, that perpetual motion machines of the second kind are impossible.
- The third law of thermodynamics refers to the entropy of a system at absolute zero temperature ($T = 0$) and states that it is impossible to lower T in such a manner that reaches the limit $T = 0$.

Classical thermodynamics accounts for the exchange of work and heat between systems with emphasis in states of thermodynamic equilibrium. Thermal equilibrium is a condition *sine qua non* for *macroscopically specified systems* only. It shoul be noted that, at the microscopic (atomic) level all physical systems undergo random fluctuations. Every finite system will exhibit statistical fluctuations in its thermodynamic variables of state (entropy, temperature, pressure, etc.), but these are negligible for macroscopically specified systems. Fluctuations become important for microscopically specified systems. Exceptionally, for macroscopically specified systems found at critical states, fluctuations are of the essence.

1.2. The Legendre transform

The Legendre transform is an operation that transforms one real-valued function of f a real variable x into another f_T, of a different variable y, maintaining constant its information

content. The derivative of the function f becomes the argument to the function f_T.

$$f_T(y) = xy - f(x);\ \ y = f'(x) \Rightarrow \text{ reciprocity.} \tag{1}$$

The Legendre transform its own inverse. It is used to get from Lagrangians the Hamiltonian formulation of classical mechanics.

Legendre' reciprocity relations constitute thermodynamics' essential formal ingredient [2]. In general, for two functions I and α one has

$$I(A_1, \ldots, A_M) \ = \ \alpha + \sum_{k=1}^{M} \ \lambda_k A_k, \tag{2}$$

with the A_i extensive variables and the λ_i intensive ones. Obviously, the Legendre transform main goal is that of changing the identity of our relevant independent variables. For α we have

$$\alpha(\lambda_1, \ldots, \lambda_M) = I - \sum_{k=1}^{M} \ \lambda_k \left\langle A_k \right\rangle . \tag{3}$$

The three operative reciprocity relations become [2]

$$\frac{\partial \alpha}{\partial \lambda_k} = -\langle A_k \rangle \ ; \qquad \frac{\partial I}{\partial \langle A_k \rangle} \ = \ \lambda_k \ ; \qquad \frac{\partial I}{\partial \lambda_i} = \sum_{k}^{M} \lambda_k \frac{\partial \langle A_k \rangle}{\partial \lambda_i}, \tag{4}$$

the last one being the so-called Euler theorem.

1.3. The axioms of thermodynamics

Thermodynamics can be regarded as a formal logical structure whose *axioms* are empirical facts [2], which gives it a unique status among the scientific disciplines [1]. The four axioms given below are equivalent to the celebrated laws of thermodynamics of the prevous Subsection [2].

- For every system there exists a quantity E, the internal energy, such that a unique E_s-value is associated to each and every state s. The difference $E_{s1} - E_{s2}$ for two different states s_1 and s_2 in a closed system is equal to the work required to bring the system, while adiabatically enclosed, from one state to the other.
- There exist particular states of a system, the equilibrium ones, that are uniquely determined by E and by a set of extensive macroscopic parameters A_ξ, $\xi = 1, \ldots, M$. The number and characteristics of the A_ξ depends on the nature of the system.
- For every system there exists a state function $S(E, \forall A_\xi)$ that (i) always grows if internal constraints are removed and (ii) is a monotonously (growing) function of E. S remains constant in quasi-static adiabatic changes.

- S and the temperature $T = [\frac{\partial E}{\partial S}]_{A_1,\ldots,A_M}$ vanish for the state of minimum energy and are non-negative for all other states.

From the second and 3rd. Postulates one extracts the following two essential assertions

1. **Statement 3a)** for every system there exists a state function S, a function of E and the A_ξ

$$S = S(E, A_1, \ldots, A_M). \tag{5}$$

2. **Statement 3b)** S is a monotonous (growing) function of E, so that one can interchange the roles of E and S in (5) and write

$$E = E(S, A_1, \ldots, A_M), \tag{6}$$

Eq. (6) clearly indicates that

$$dE = \frac{\partial E}{\partial S}\, dS + \sum_\xi \frac{\partial E}{\partial A_\xi}\, dA_\xi \Rightarrow dE = TdS + \sum_\xi P_\xi dA_\xi, \tag{7}$$

with P_ξ generalized pressures and the temperature T defined as [2]

$$T = \left(\frac{\partial E}{\partial S}\right)_{[\forall A_\xi]}. \tag{8}$$

Eq. (7) will play a key-role in our future considerations. If we know $S(E, A_1, \ldots, A_n)$ or, equivalently because of monotonicity, $E(S, A_1, \ldots, A_n)$) we have a *complete* thermodynamic description of a system [2]. For experimentalists, it is often more convenient to work with *intensive* variables defined as follows [2].

Let $S \equiv A_0$. The intensive variable associated to the extensive A_i, to be called P_i are the derivatives

$$P_0 \equiv T = [\frac{\partial E}{\partial S}]_{A_1,\ldots,A_n}, \;\; 1/T = \beta. \tag{9}$$

$$P_j \equiv \lambda_j / T = [\frac{\partial E}{\partial A_j}]_{S,A_1,\ldots,A_{j-1},A_{j+1},\ldots,A_n}. \tag{10}$$

Any one of the Legendre transforms that replaces any s extensive variables by their associated intensive ones (β, λ's will be Lagrange multipliers in SM)

$$L_{r_1,\ldots,r_s} = E - \sum_j P_j\, A_j, \;\; (j = r_1, \ldots, r_s)$$

contains the same information as either S or E. The transform $L_{r_1,\ldots,r_s}$ is a function of $n - s$ extensive and s intensive variables. This is called the *Legendre invariant structure of thermodynamics*. As we saw above, this implies certain relationships amongst the relevant

system's variables, called the *reciprocity relations* (RR), that are crucial for the microscopic discussion of Thermodynamics.

2. Classical statistical mechanics

In 1903 Gibbs formulated the first axiomatic theory for statistical mechanics [1, 3], revolving around the concept of phase space. The phase space (PS) precise location is given by generalized coordinates and momenta. Gibbs' postulates properties of an imaginary (Platonic) ad-hoc notion: the "ensemble" (a mental picture). The ensemble consists of extremely many (N) independent systems, all identical in nature with the one of actual physical interest, but differing in PS-location. That is, the original system is to be mentally repeated many times, each with a different arrangement of generalized coordinates and momenta. Here Liouville's theorem of volume conservation in phase space for Hamiltonian motion plays a crucial role. The ensemble amounts to a distribution of N PS-points, representative of the actual system. N is large enough that one can properly speak of a density D at any PS-point $\phi = q_1, \ldots, q_N; p_1, \ldots, p_N$, with $D = D(q_1, \ldots, q_N; p_1, \ldots, p_N, t) \equiv D(\phi)$, with t the time, and, if we call $d\phi$ the volume element,

$$N = \int d\phi\, D; \quad \forall \text{t}. \tag{11}$$

Randomly extracting a system from the ensemble, the probability of selecting it being located in a neighborhood of ϕ would yield

$$P(\phi) = D(\phi)/N. \tag{12}$$

Consequently,

$$\int P\, d\phi = 1. \tag{13}$$

Liouville's theorem follows from the fact that, since phase-space points can not be "destroyed", if

$$N_{12} = \int_{\phi_1}^{\phi_2} D\, d\phi, \tag{14}$$

then

$$\frac{dN_{12}}{dt} = 0. \tag{15}$$

An appropriate analytical manipulation involving Hamilton's canonical equations of motion then yields the theorem in the form [1]

$$\dot{D} + \sum_i^N \frac{\partial D}{\partial p_i}\, \dot{p}_i + \sum_i^N \frac{\partial D}{\partial q_i}\, \dot{q}_i = 0, \tag{16}$$

entailing the PS-conservation of density.

Equilibrium means simply $\dot{D} = 0$, i. e.,

$$\sum_i^N \frac{\partial D}{\partial p_i}\, \dot{p}_i + \sum_i^N \frac{\partial D}{\partial q_i}\, \dot{q}_i = 0. \tag{17}$$

2.1. The classical axioms

Gibbs refers to PS-location as the “phase" of the system [1, 3]. The following statements completely explain in microscopic fashion the corpus of classical equilibrium thermodynamics [1].

- The probability that at time t the system will be found in the dynamical state characterized by ϕ equals the probability $P(\phi)$ that a system randomly selected from the ensemble shall possess the phase ϕ will be given by Eq. (12) above.
- All phase-space neighborhoods (cells) have the same a priori probability.
- D depends only upon the system’s Hamiltonian.
- The time-average of a dynamical quantity F equals its average over the ensemble, evaluated using D.

3. Information

Information theory (IT) treats information as data communication, with the primary goal of concocting efficient manners of encoding and transferring data. IT is a branch of applied mathematics and electrical engineering, involving the quantification of information, developed by Claude E. Shannon [4] in order to i) find fundamental limits on signal processing operations such as compressing data and ii) finding ways of reliably storing and communicating data. Since its 1948-inception it has considerably enlarged its scope and found applications in many areas that include statistical inference, natural language processing, cryptography, and networks other than communication networks. A key information-measure (IM) was originally called (by Shannon) entropy, in principle unrelated to thermodynamic entropy. It is usually expressed by the average number of bits needed to store or communicate one symbol in a message and quantifies the uncertainty involved in predicting the value of a random variable.Thus, a degree of knowledge (or ignorance) is associated to any normalized probability distribution $p(i)$, $(i = 1, \ldots, N)$, determined by a functional $I[\{p_i\}]$ of the $\{p_i\}$ [4–7] which is precisely Shannon’s entropy. IT was la axiomatized in 1950 by Kinchin [8], on the basis of four axioms, namely,

- I is a function ONLY of the $p(i)$,
- I is an absolute maximum for the uniform probability distribution,
- I is not modified if an $N+1$ event of probability zero is added,
- Composition law.

As for the last axiom, consider two sub-systems $[\Sigma^1,\ \{p^1(i)\}]$ and $[\Sigma^2,\ \{p^2(j)\}]$ of a composite system $[\Sigma,\ \{p(i,j)\}]$ with $p(i,j) = p^1(i)\, p^2(j)$. Assume further that the conditional probability distribution (PD) $Q(j|i)$ of realizing the event j in system 2 for a fixed $i-$event in system 1. To this PD one associates the information measure $I[Q]$. Clearly,

$$p(i,j) = p^1(i)\, Q(j|i). \tag{18}$$

Then Kinchin’s fourth axiom states that

$$I(p) = I(p^1) + \sum_i p^1(i)\, I\big(Q(j|i)\big). \tag{19}$$

An important consequence is that, out of the four Kinchin axioms one finds that Shannons's measure

$$S = -\sum_{i=1}^{N} p(i) \ln [p(i)], \tag{20}$$

gives us the only way of complying with Kinchin's axioms.

4. Statistical mechanics and information theory

It has been argued [9] that the statistical mechanics (SM) of Gibbs is a juxtaposition of subjective, probabilistic ideas on the one hand and objective, mechanical ideas on the other. From the mechanical viewpoint, the vocables "statistical mechanics" suggest that for solving physical problems we ought to acknowledge a degree of uncertainty as to the experimental conditions. Turning this problem around, it also appears that the purely statistical arguments are incapable of yielding any physical insight unless some mechanical information is a priori assumed [9]. This is the conceptual origin of the link SM-IT pioneered by Jaynes in 1957 via his Maximum Entropy Principle (MaxEnt) [5, 6, 10] which allowed for reformulating SM in information terms. Since IT's central concept is that of information measure (IM)

Descartes' scientific methodology considers that truth is established via the agreement between two *independent* instances that can neither suborn nor bribe each other: analysis (purely mental) and experiment [11]. The analytic part invokes mathematical tools and concepts: Mathematics' world $\Leftrightarrow$ Laboratory. The mathematical realm is called Plato's Topos Uranus (TP). Science in general, and physics in particular, may thus be seen as a [TP $\Leftrightarrow$ "Experiment"] two-way bridge. TP concepts are related to each other in the form of "laws" that adequately describe the relationships obtaining among suitable chosen variables that describe the phenomenon at hand. In many cases these laws are integrated into a comprehensive theory (e.g., classical electromagnetism, based upon Maxwell's equations) [1, 12–15].

Jaynes' MaxEnt ideas describe thermodynamics via the link [IT as a part of TP]$\Leftrightarrow$ [Thermal experiment], or in a more general scenario: [IT] $\Leftrightarrow$ [Phenomenon at hand]. It is clear that the relation between an information measure and entropy is [IM] $\Leftrightarrow$ [Entropy S]. One can then assert that an IM is not necessarily an entropy, since the first belongs to the Topos Uranus and the later to the laboratory. Of course, in some special cases an association $IM \Leftrightarrow$ entropy S can be established. Such association is both useful and proper in very many situations [5].

If, in a given scenario, N distinct outcomes ($i = 1, \ldots, N$) are possible, three alternatives are to be considered [6]:

1. Zero ignorance: predict with certainty the actual outcome.
2. Maximum ignorance: Nothing can be said in advance. The N outcomes are equally likely.

3. Partial ignorance: we are given the probability distribution $\{P_i\}$; $i = 1, \ldots, N$.

If our state of knowledge is appropriately represented by a set of, say, M expectation values, then the "best", least unbiased probability distribution is the one that [6]

- reflects just what we know, without "inventing" unavailable pieces of knowledge [5, 6] and, additionally,
- maximizes ignorance: the truth, all the truth, *nothing but* the truth [6].

Such is the MaxEnt rationale. In using MaxEnt, one is not maximizing a physical entropy, but only maximizing ignorance in order to obtain the least biased distribution compatible with the a priori knowledge.

Statistical mechanics and thereby thermodynamics can be formulated on an information theory basis if the density operator $\hat{\rho}$ is obtained by appealing to Jaynes' maximum entropy principle (MaxEnt), that can be stated as follows:

Assume that your prior knowledge about the system is given by the values of M expectation values $< A_1 >, \ldots, < A_M >$. In such circumstances $\hat{\rho}$ is uniquely determined by extremizing $I(\hat{\rho})$ subject to M constraints given, namely, the M conditions $< A_j >= Tr[\hat{\rho}\, \hat{A}_j]$, a procedure that entails introducing M Lagrange multipliers λ_i. Additionally, since normalization of $\hat{\rho}$ is necessary, a normalization Lagrange multiplier ξ should be invoked. The procedure immediately leads one [6] to realizing that $I \equiv S$, the equilibrium Boltzmann's entropy, if the a priori knowledge $< A_1 >, \ldots, < A_M >$ refers only to extensive quantities. Of course, I, once determined, *affords for complete thermodynamical information for the system of interest* [6].

5. A new micro-macroscopic way of accounting for thermodynamics

Gibbs' and MaxEnt approaches satisfactorily describe equilibrium thermodynamics. We will here search for a new, different alternative able to account for thermodynamics from first principles. Our idea is to give axiom-status to Eq. (7), *which is an empirical statement*. Why? Because neither in Gibbs' nor in MaxEnt's axioms we encounter a direct connection with actual thermal data. By appealing to Eq. (7) we would instead be actually employing empirical information. This is our rationale.

Consequently, we will concoct a new SM-axiomatics by giving postulate status to the following macroscopic statement:

Axiom (1)

$$dE = TdS + \sum_{\nu} P_\nu dA_\nu. \tag{21}$$

This is a macroscopic postulate to be inserted into a microscopic axiomatics' corpus.

We still need *some* amount of microscopic information, since we are building up a microscopic theory. We wish to add as little as possible, of course (Ockham's razor). At this point it is useful to remind the reader of Kinchin's postulates, recounted above. We will content ourselves with borrowing for our theoretical concerns just his his first axiom. Thus, we conjecture at this point, and will prove below, that the following assertion suffices for our theoretical purposes:

Axiom (2) If there are W microscopic accessible states labelled by i, whose microscopic probability we call p_i, then

$$S = S(p_1, p_2, \ldots, p_W). \tag{22}$$

Thus, we are actually taking as a postulate something that is actually known from both quantum and classical mechanics.

Axiom (3) The internal energy E and the external parameters A_ν are to be considered as the expectation values of suitable operators, that is, the hamiltonian H and the hermitian operators $\mathcal{R}_\nu$ (i.e., $A_\nu \equiv < \mathcal{R}_\nu >$). Thus, the A_ν (and also E) will depend on the eigenvalues of these operators *and* on the probability set. (Note that energy eigenvalues depend of course upon the $\mathcal{R}_\nu$.

The reader will immediately realize that Axiom (2) is just a way of re-expressing Boltzmann's "atomic" conjecture. Thus, macroscopic quantities become statistical averages evaluated using a microscopic probability distribution [16]. Our present three new axioms are statements of fact. What do we mean? That they are borrowed from either experiment or pre-existent theories. Somewhat surprisingly, our three axioms do not actually incorporate any knew knowledge at all. The merely re-express known previous notions. Ockham's razor at its best! Our theory could no be more economical.

We need now to prove that the above three postulates allow one to reconstruct the imposing edifice of statistical mechanics. We will tackle this issue by showing below that they our axioms are equivalent to those of Jaynes' [17]. At this point we need to recall the main goal of statistical mechanics, namely, finding the probability distribution (or the density operator) that best describes our physical system. In order to do so Jaynes appealed to his MaxEnt postulate, that we restate below for the sake of fixing notation.

MaxEnt axiom: assume your prior knowledge about the system is given by the values of M expectation values

$$A_1 \equiv < \mathcal{R}_1 >, \ldots, A_R \equiv < \mathcal{R}_M > . \tag{23}$$

Then, ρ is uniquely fixed by extremizing the information measure $I(\rho)$ subject to $\rho-$normalization plus the constraints given by the M conditions constituting our assumed foreknowledge

$$A_\nu = < \mathcal{R}_\nu > = Tr[\rho\, \mathcal{R}_\nu]. \tag{24}$$

This leads, after a Lagrange-constrained extremizing process, to the introduction of M Lagrange multipliers λ_ν, that one assimilates to the generalized pressures P_ν. The truth, the whole truth, nothing but the truth [6]. Jaynes rationale asserts that if the entropic measure that reflects our ignorance were not of maximal character, we would actually be *inventing* information not at hand.

While working through his variational process, Jaynes discovers that, after multiplying by Boltzmann's constant k_B the right-hand-side of his expression for the information measure, it converts itself into an entropy, $I \equiv S$, the equilibrium thermodynamic one, with the caveat that $A_1 = < \mathcal{R}_1 >, \ldots, A_M = < \mathcal{R}_M >$ refer to extensive quantities. Having ρ, his universal form $I(\rho)$ *yields complete microscopic information with respect to the system of interest*. To achieve our ends one needs now just to prove that the new axiomatics, with (21) and (22), is equivalent to MaxEnt.

6. New connection between macroscopic and microscopic approaches

In establishing our new connections between the micro- and macro-scenarios we shall work with the classical instance only, since the corresponding quantum treatment constitute in this sense just a straightforward extension.

Our main idea is to pay attention to the generic change $p_i \to p_i + dp_i$ as constrained by Eq. (21). In other word, we insist on studying the change dp_i that takes place in such a manner that (21) holds. Our main macroscopic quantities S, A_j, and E will vary with dp_i. These changes are not arbitrary but are constrained by (21). Note here an important advantage to be of our approach. We need *not* specify beforehand the information measure employed.

Since several possibilities exist (see for instance Gell-Mann and Tsallis [18]), this entails that the choice of information nature is not predetermined by macroscopic thermodynamics. For a detailed discussion of this issue see Ferri, Martinez, and Plastino [19].

The pertinent ingredients at hand are

- an arbitrary, smooth function $f(p)$ permitting one expressing the information measure via

$$I \equiv S(\{p_i\}) = \sum_i p_i\, f(p_i), \tag{25}$$

  such that $S(\{p_i\})$ is a concave function,
- M quantities A_ν representing values of extensive quantities $\langle \mathcal{R}_\nu \rangle$, that adopt, for a micro-state i, the value a_i^ν with probability p_i,
- still another arbitrary smooth, monotonic function $g(p_i)$ ($g(0) = 0$; $g(1) = 1$). With the express purpose of employing generalized, non-Shannonian entropies, we slightly generalize here the expectation-value definitions by recourse to g via (26):

$$A_\nu \equiv \langle \mathcal{R}_\nu \rangle = \sum_i^W a_i^\nu\, g(p_i);\ \ \nu = 2, \ldots, M, \tag{26}$$

$$E = \sum_i^W \epsilon_i\, g(p_i), \tag{27}$$

  where ϵ_i is the energy associated to the microstate i.

We take $A_1 \equiv E$ and pass to a consideration of the probability variations dp_i that should generate accompanying changes dS, dA_ν, and dE in, respectively, S, the A_ν, and E.

The essential issue at hand is that of enforcing compliance with

$$dE - TdS + \sum_{\nu=1}^W dA_\nu \lambda_\nu = 0, \tag{28}$$

with T the temperature and λ_ν generalized pressures. By recourse to (25), (26), and (27) we i) recast now (28) for

$$p_i \to p_i + dp_i, \tag{29}$$

and ii) expand the resulting equation up to first order in the dp_i.

Remembering that the Lagrange multipliers λ_ν are identical to the generalized pressures P_ν of Eq. (7), one thus encounter, after a little algebra [20–26],

$$\begin{gathered} C_i^{(1)} = [\sum_{\nu=1}^{M} \lambda_\nu \, a_i^\nu + \epsilon_i] \\ C_i^{(2)} = -T \frac{\partial S}{\partial p_i} \\ \sum_i [C_i^{(1)} + C_i^{(2)}] dp_i \equiv \sum_i K_i dp_i = 0, \end{gathered} \tag{30}$$

so that, appropriately rearranging things

$$\begin{gathered} T_i^{(1)} = f(p_i) \; + \; p_i \, f'(p_i) \\ T_i^{(2)} = -\beta[(\sum_{\nu=1}^{M} \lambda_\nu \, a_i^\nu + \epsilon_i) \, g'(p_i) - K], \\ (\beta \equiv 1/kT), \end{gathered} \tag{31}$$

and we are in a position to recast (30) in the fashion

$$T_i^{(1)} + T_i^{(2)} = 0; \;\; (for \;\; any \;\; i), \tag{32}$$

an expression whose importance will become manifest later on.

Eqs. (30) or (32) yield one and just one p_i-expression, as demonstrated in Refs. [20–26]. However, it will be realized below that, at this stage, an explicit expression for this probability distribution is not required.

We pass now to traversing the opposite road that leads from Jaynes' MaxEnt procedure and ends up with *our* present equations. This entails extremization of S subject to constraints in E, A_ν, and normalization. For details see [20–26].

Setting $\lambda_1 \equiv \beta = 1/T$ one has

$$\delta_{p_i}[S - \beta \langle H \rangle - \sum_{\nu=2}^{M} \lambda_\nu \langle \mathcal{R}_\nu \rangle - \xi \sum_i p_i] = 0, \tag{33}$$

(normalization Lagrange multiplier ξ) is easily seen in the above cited references to yield as a solution the very set of Eqs. (30). The detailed proof is given in the forthcoming Section. Eqs. (30) arise then from two different approaches:

- our methodology, based on Eqs. (21) and (22), and
- following the well known MaxEnt route.

Accordingly, we see that both MaxEnt and our axiomatics co-imply one another. They are indeed equivalent ways of constructing equilibrium statistical mechanics. As a really relevant fact

One does not need to know the analytic form of $S[p_i]$ neither in Eqs. (30) nor in (33).

7. Proof

Here we prove that Eqs. (30) can be derived from the MaxEnt approach (33). One wishes to extremize S subject to the constraints of fixed valued for i) U, ii) the M values A_ν (entailing Lagrange multipliers (1) β and (2) M γ_ν), and iii) normalization (Lagrange multiplier ξ). One has also

$$A_\nu = \langle \mathcal{R}_\nu \rangle = \sum_i p_i \, a_i^\nu , \tag{34}$$

with $a_i^\nu = \langle i|\mathcal{R}_\nu|i\rangle$ the matrix elements in the basis $\langle i\rangle$ of $\mathcal{R}_\nu$. The ensuing variational problem one faces, with $U = \sum_i \, p_i \epsilon_i$, is

$$\delta_{\{p_i\}} \left[S - \beta U - \sum_{\nu=1}^{M} \gamma_\nu A_\nu - \xi \sum_i p_i \right] = 0, \tag{35}$$

that immediately leads, for $\gamma_\nu = \beta \lambda_\nu$, to

$$\delta_{p_m} \sum_i \left(p_i f(p_i) - [\beta p_i (\sum_{\nu=1}^{M} \lambda_\nu \, a_i^\nu + \epsilon_i) + \xi p_i] \right) = 0, \tag{36}$$

so that the the following two quantities vanish

$$f(p_i) + p_i f'(p_i) - [\beta(\textstyle\sum_{\nu=1}^{M} \lambda_\nu \, a_i^\nu + \epsilon_i) + \xi]$$

$$\Rightarrow \text{ if } \xi \equiv \beta K,$$

$$f(p_i) + p_i f'(p_i) - \beta(\textstyle\sum_{\nu=1}^{M} \lambda_\nu a_i^\nu + \epsilon_i) + K]$$

$$\Rightarrow 0 = T_i^{(1)} + T_i^{(2)}. \tag{37}$$

We realize now that (32) and the last equality of (37) are one and the same equation. MaxEnt does lead to (32).

8. Conclusions

We have formally proved above that our axiomatics allows one to derive MaxEnt equations and viceversa. Thus, our treatment provides an alternative foundation for equilibrium statistical mechanics. We emphasized that, opposite to what happens with both Gibbs' and Jaynes' axioms, our postulates have zero new informational content. Why? Because they are borrowed either from experiment or from pre-existing theories, namely, information theory and quantum mechanics.

The first and second laws of thermodynamics are two of physics' most important empirical facts, constituting pillars to our present view of Nature. Statistical mechanics (SM) adds an underlying microscopic substratum able to explain not only these two laws but the whole of thermodynamics itself [2, 6, 27–30]. Basic SM-ingredient is a microscopic probability

distribution (PD) that controls microstates-population [27]. Our present ideas yield a detailed picture, from a new perspective [20–26], of how changes in the independent external thermodynamic parameters affect the micro-state population and, consequently, the entropy and the internal energy.

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