Ergodic hypothesis and Boltzmann's equation

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Abstract: *On the Ergodic hypothesis, Ensembles and Boltzmann's equation (B.E.): few comments on selected papers by Boltzmann (preceding (B.E.)) and by Maxwell (preceding and following it).*

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Many excellent (classic and contemporary) analysis exist on the birth of the ergodic hypothesis: by looking again to the original works of Boltzmann, Clausius and Maxwell preceding the derivation of the B.E. and the H-theorem might be nevertheless worth. Here are collected and briefly illustrated ideas and remarks that I exposed in several publications with a few additions.

I. 1866

Referring to the "second law":

$$\frac{dQ}{T} =' exact' \qquad \& \qquad \oint \frac{dQ}{T} \le 0$$

in 1866 Boltzmann proposes, [1], that the second law, *"over a cyclic process in which "actions and reactions are equal to each other, so that in the interior of the body either thermal equilibrium or a stationary heat flow will always be found"*, reflects a very general "theorem" of mechanics and argues as follows:

1) By an earlier mechanical argument, by Krönig, [2], temperature is identified with the time-averaged kinetic energy.
2) A proof is then set up towards a result "entirely coincident" with Clausius' law (1857), [3], adding a basic assumption, [1, p.24]:

"An arbitrarily selected atom runs over every site of the region occupied by the body in a suitable time interval (no matter if very long), of which the instants t_1 and t_2 are the initial and final times, at the end of which the speeds and the directions come back to the original value in the same location, describing a closed curve and repeating, from this instant on, their motion."

Fundamentally motions are periodic: implying that averages of observables are computed simply by integrating over the period of a motion $t \to x(t)$ developing, with period i ,[1] kinetic energy $K(x) = \frac{1}{2}\dot{x}^2$, under forces with potential $V(x) = V_{int}(x) + V_{ext}(x)$.

Problem: Consider the variation of the averages of the kinetic energy and of potential energy when an equilibrium state orbit changes from $x(t)$ to $x(t) + \delta x(t)$.

Let $x(t) = \xi(\frac{t}{i})$ with $\xi(\varphi)$ 1-periodic, and represent the averages of an observable $F(x)$ and of the kinetic energy $K(x)$ as:

$$\overline{F} = \frac{1}{i}\int_0^i F(x(t'))dt' \equiv \int_0^1 F(\xi(\varphi))d\varphi,$$
$$\overline{K} = \frac{1}{2}\int_0^1 \frac{\xi'(\varphi)^2}{i^2}d\varphi$$

and imagine the variations of x in terms of those of i ad ξ.

Changing x by δx means to change ξ by $\delta\xi$ and i by δi. So the variation of an average is the sum of the variation due to $\delta\xi$ and that due to δi: $\delta\overline{F} = \delta_\xi\overline{F} + \delta_i\overline{F}$:

$$\delta\overline{V} \equiv \delta_\xi\overline{V},\ \delta\overline{K} = -2\frac{\delta i}{i}\overline{K} + \delta_\xi\overline{\overline{K}}$$

The variation $\delta(\overline{K} + \overline{V}) \stackrel{def}{=} \delta\overline{U}$ has a natural interpretation:

$$\delta(\overline{K} + \overline{V}) = \delta(\overline{K} + \overline{V}_{int}) + \delta\overline{V}_{ext} = \delta\overline{U} + \delta\overline{L} \equiv \delta Q$$

with δQ interpreted as heat in/out in the process $x \to x'$.

But keeping in mind $\delta\overline{K} = -2\frac{\delta i}{i}\overline{K} + \delta_\xi\overline{K}$:

$$\delta Q \equiv \delta(\overline{K} + \overline{V}) = -2\frac{\delta i}{i}\overline{K} + \delta_\xi(\overline{K} + \overline{\overline{V}})$$
$$= -2\frac{\delta i}{i}\overline{K} + 2\delta_\xi\overline{K} + \delta_\xi(-\overline{K} + \overline{V}) \equiv +2\frac{\delta i}{i}\overline{K} + 2\delta\overline{K} + 0$$

by Maupertuis' principle (applied to the variation of the average action $-\overline{K} + \overline{V}$ *at fixed period*).

Therefore, (*Heat theorem*):

$$\frac{\delta Q}{\overline{K}} = +2\frac{\delta i}{i} + 2\frac{\delta\overline{K}}{\overline{K}} = 2\delta\log(i\overline{K}) \stackrel{def}{=} \delta\mathbf{S}$$

is an exact differential.

Remarks

i) the above presentation is the later one of Clausius, [4]: which not only is easier to read, but also takes into account the possibility of existence of external work, not considered by Boltzmann. This point was stressed by Clausius in [5] to whom Boltzmann had pointed out the "identity" of [4] with [1]: Boltzmann acknowledged but stated that his more involved argument would apply also in presence of external work, [6].

ii) Boltzmann: *..The second fundamental law is related to a theorem of pure mechanics to which it corresponds just as the "vis viva" principle corresponds to the first principle.... in a somewhat generalized form."*, [1, #2,sec.IV]. The *vis viva* principle is Maupertuis' principle.

iii) Should it be assumed that Boltzmann, Clausius, Maxwell, ... were really believing that the continuous

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[1]Here the original, now unusual, notation i is kept.

path described, in the $6N-1$ phase space, by the system really filled the entire continuum ? which is a form of 'ergodic hypothesis'. I think that is not possible to say so, in spite of a strictly literal interpretation of Maxwell's (1879):

.. but we may with considerable confidence assert that except for particular forms of the surface of the fixed obstacle, the system will sooner or later, after a sufficient number of encounters, pass through every phase consistent with the equation of energy. [7].

In fact Boltzmann presented philosophical ideas (see [8, p.55,56],[9, p.146], also [10, 11]) that unequivocally indicate that he must have conceived that a "phase point" is not a "geometric point" but as a small 'box' in a $6N$-dim space: a heuristic view consistent with the possibility that a moving point could visit the whole energy surface in phase space. And Maxwell followed.

II. 1868

Boltzmann was certainly worried more by the periodicity assumption and well before the (1870) priority controversy with Clausius, [5], concentrated on describing stationary states.

The *breakthrough* 1868 work begins: *...finally I shall establish a general theorem on the probability that the considered point masses occupy distinct locations and velocities*, [12].

Forgetting periodicity supposes that the distribution $f(\mathbf{p},\mathbf{q})$ is a smooth function on phase space, which is covered densely by the point. Then the Liouv. th. **"implies"** constancy of f. Maxwell will comment (1879):

But whether we are able or not to prove that the constancy of this function is a necessary condition of a steady distribution, it is manifest that if the function is initially constant for all phases consistent with the equation of energy, it will remain so during the motion. This therefore is one solution, if not the only solution, of the problem of a steady distribution.

Boltzmann proceeds further to derive explicitly the Maxwellian for the velocities and introduces a method to count the occupation number of phase space cells: by dividing phase space into equal volume cells this is obtained by the now familiar counting argument; consistency with stationarity rests on the conservation of their volume (*i.e.* Liouville's theorem), [12]. The result is expressed for N particles enclosed in a vessel Ω subject to an interaction potential χ as:

$$f(\mathbf{p},\mathbf{q}) = const\,\delta(\frac{1}{2}\mathbf{p}^2+\chi(\mathbf{q})-N\kappa)d^{3N}\mathbf{p}d^{3N}\mathbf{q}$$

i.e. (in modern notation, [10]) microcanonical ensemble.

The achievement induced Boltzmann to look for an example in which most trajectories would at least be dense on the energy surface: the example, [13], turned out not to fulfill even this "weaker property" (see [10, Appendix D], and a proof in [14]).

The example shows that Boltzmann did not yet conceive the possible existence of other probability distributions with positive density on the region of phase space allowed by the values of other constants of motion beyond the energy.

III. 1871

The viewpoint changes (1871) in the "trilogy", *i.e.* in three basic papers [15–17], developing the ideas of 1868, where he became very concerned about it.

(I), [15], Derives the microcanonical distribution for the atoms of a single molecule in a gas. This is not obtained by supposing the particles energies discretized regularly, as done in [12], but exploiting invariance properties.

The central theme, implicit in the 1868 paper, in B. emerges here: a) equilibrium distribution has a density in phase space, b) symplectic symmetry $\Rightarrow$ volume element is conserved (surprisingly unaware of Liouville's theorem it is checked repeatedy also in eralier and later works, where several dense pages could have been spared), c) adding the assumption of rarefied gas (as multiple molecular collisions are neglected).

If the trajectories are dense in phase space and the distribution is continuous it has to be a function of the energy (invariant by Liouville).

(II), [16], Not only goes beyond the no multiple collisions assumptions and applies to any denstity.

The general system is as a "giant molecule" and, from the idea in I) (applied to the molecules of a gas), the statistics is found by considering a large number of copies of the system without reciprocal interaction.

Density of trajectories in phase space is still taken for granted but its dependence on the only energy is openly questioned, and absence of multiple collisions or of other constants of motion added as supporting assumptions.

(III), [16], This is the first introduction of the notion of "thermodynamic analogy" or "model of thermodynamics": an example is exhibited by the canonical distribution (reference to periodicity is formally avoided).

Define dQ, the heat received, as the variation of the total average energy dE plus the work dW, computed varying among stationary distributions in a family describing the stationary states: then if $\frac{dQ}{T}$ is exact the distributions constitute a model of thermodynamics. Example: the microcanonical ensemble.

As recognized by Gibbs, [18], II & III yield the foundation of the theory of the ensembles.

IV. 1872 & 1879

The next step has been the development of Boltzmann's equation, (B.E.), [19]. It provided, at least for rarefied gases, a quantitative method to estimate the macroscopic times in the irreversible approach to equilibrium.

It also allowed to determine macroscopic equations obeyed by gases. It could be said that the major achievement was the H-theorem derivation.

In this respect it is interesting to read the 1879 paper of Maxwell, one of the last in his life, entirely dedicated to comment the 1868 Boltzmann's, [7].

However the long and detailed analysis celebrating the Boltzmann's 1868 work, not even quoting his 1872 well known paper on B.E., states:

"His method of treatment is ingenious, and, as far as I can see, satisfactory, but I think that a problem of such primary importance in molecular science ought to be scrutinized and examined on every side, so that as many persons as possible may be enabled to follow the demonstration, and to know on what assumptions it rests."

Why did Maxwell "overlook" B.E. contribution? A possible explanation is that he had greatly contributed to the theory of gases: his work "On the dynamical theory of gases", [20], is a major contribution motivated by his interest on the nature of viscosity.

Maxwell had built, (1860-1866), a general theory of rarefied gases macroscopic properties via the study of the evolution of various observables under the influence of Hamiltonian dynamics with r^{-5} interparticle interaction (earlier considered elastic hard balls, [21]).

In each case evolution was studied via the analysis of the collisions or scattering: techniques & results were what would be obtained, on a case by case basis, by integrating the B.E. after multiplying both sides by the observable of interest.

His had been a "weak version of B.E.". Exactly applied as is still followed when applying the B.E.

So I dare to think that Maxwell felt that the paper of 1868 was the main breakthrough of B., leading to a very general theory of equilibrium based on the ergodic hypothesis.

The H-theorem was a synthesis over many studies clarifying the irreversibility phenomenon: with time it exercized essential influence to extend the role of entropy on modern studies on stationary nonequilibrium, dominated by the role of strange attractors, [22–25], in our modern understanding of irreversibility.

See [10, 26] for comments and partial transl. of B.'s works.

Note: This is a text deriving from a talk for the conference "150 years from the publication of the paper by Ludwig Boltzmann containing his celebrated equation and the related H-theorem", 29-30 November 2022, at the Center for Mathematical Research "Ennio De Giorgi" of the Scuola Normale Superiore di Pisa.

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