Ergodicity: a historical perspective. Equilibrium and Nonequilibrium

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Abstract

A view on the physical meaning of the so called ergodic hypothesis: its role on the foundations of equilibrium statistical mechanics in mid '1800, its interpretations and hints at its relevance for modern nonequilibrium statistical mechanics. Followed by appendices with detailed comments on the original papers.

Keywords: Ergodicity, Chaotic hypothesis, Gibbs distributions, SRB distributions

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Original Boltzmann papers, and their pages, are quoted by their number, and page numbers, in the *Wissenshaeftliche Abhandlungen* (WA). Appendices with comments to original papers usually follow a few partial translations.

"The entropy of the universe is always increasing" *is not a very good statement of the second law*, **[Feynman et al., 1963, Sec. 44.12]: this is Feynman.**[1]
Clausius' formulation of the second law is "*It is impossible to construct a device that, operating in a cycle will produce no effect other than the transfer of heat from a cooler to a hotter body***", [Zemansky, 1957, p.148]**.
Existence of equilibrium entropy follows as a theorem: Clausius' "fundamental theorem of the theory of heat", here "heat theorem". Is there an analogue of Ergodic Hypothesis and Entropy in nonequilibrium thermodynamics?

Some terminology: The "ergodic hypothesis" in the sense of Boltzmann and Maxwell is that, in a confined Hamiltonian system, "a phase space point evolves in time and eventually visits all other points with the same energy" [2] (aside from obvious exceptions due to symmetries or to integrability of the motions, like for harmonic chains): but this can make sense only if the phase space is considered discrete and finite. [3] I argue below that it is in this sense that Boltzmann and Maxwell intended the hypothesis: furthermore in Section13 I discuss how the definition, so interpreted, could be applied also to nonequilibrium situations, unifying conceptually equilibrium and nonequilibrium theories of stationary states.

1 Chronology

1866: Boltzmann establishes a relation between the least action principle and the entropy variation in a quasi static process assuming that atoms move periodically and equilibrium states are identified with collections of periodic orbits: this is a first version of the "heat theorem". Determination of the probability distribution of phase space points is not attempted, [Boltzmann, 1866, #2].

1868: In [Boltzmann, 1868a, #5] the distribution on phase space for a system of n atoms in equilibrium is defined as a probability density which is positive on the region of phase space visited by a trajectory and, at any point, it is identified as proportional to the fraction of the time spent by the trajectory near that point. The probability density is supposed, without saying, smooth (possibly

[1] Although I also think so it is safer to rely on authorities.

[2] Boltzmann and Maxwell considered systems in which the single, undisturbed motion, if pursued without limit in time, will finally traverse "every phase point" which is compatible with the given total energy, [Ehrenfest and Ehrenfest, 1990, p.21]: and Boltzmann called them "ergodic".

[3] A "quasi ergodic hypothesis", [Ehrenfest and Ehrenfest, 1990, p.90], weaker than the original, has been introduced by requiring that, aside from trivial exceptions, the trajectories of the points should cover a dense set on the energy surfaces: this eliminates the contradiction forbidding that a single continuum trajectory visits the entire energy surface. In modern Mathematics a confined Hamiltonian system is called "ergodic" on an energy surface if all its initial data, but a set of zero Liouville measure, evolve spending in any measurable set a fraction of time proportional to its measure.

aside for discontinuities due to hard cores or walls collisions) and its uniqueness is not (yet) challenged by Boltzmann, see also comments in AppendixC below. After several increasingly complex examples he obtains what is now called the *microcanonical distribution* in the $6n-1$ dimensional energy surface. As remarked by [Maxwell, 1879] the ergodic hypothesis (*i.e.* the assumption that a single trajectory visits the entire energy surface performing a periodic motion in phase space) is implicit in the argument.[4]

1871: Clausius obtains the 1866 result of Boltzmann: his work is clearer but the conclusions are the same. The matter is clarified by the following dispute on priority,[Clausius, 1871, 1872],[Boltzmann, 1871a, #17], see also comments in AppendicesA,B below.

1871: Boltzmann's 1871 "trilogy"
(a) In [Boltzmann, 1871b, #18] the distribution of the states of individual r-atomic molecules in their center of mass is studied. Density is assumed positive on the accessible regions of phase space which, because of the collisions, is "reasonably" identified with the entire $6r-6$ dimensional phase space. The further assumptions are, first, negligible collisions duration and, second, absence of multiple collisions. It is shown, extending arguments of Maxwell for monoatomic gases, that the distribution is the *canonical distribution*, as now it is called. Having neglected multiple collisions leads Boltzmann to asking wheter the distribution found is the unique stationary, see also comments in AppendixE below.

(b) Derivation of the microcanonical distribution under the *ergodic hypothesis* in [Boltzmann, 1871c, #19]: formally set here for the first time and applied to recover the results of (a) and, furthermore, to show that any large subsystem is distributed with a *canonical distribution*. In this work the question is also raised on whether the ergodic hypothesis is correct. A second aspect of this work is that for the first time an "ensemble" is used as a device to compute the statistics of the equilibria. It is remarkable that its introduction is not "by an axiom": instead it is derived from (a), the preceding work. The gas of n r-atomic molecules is considered as a collection of n identical systems of points moving independently and distributed (in their $(6r-6)$-dimensional phase space) so as to keep the global phase space density constant in time. Since (in (a)) the collision time is neglegible and multiple collisions excluded, the trajectory changes due to collisions are thought as interactions with an external warm body so that the system of molecules becomes and "ensemble". Microscopic motion is still periodic, because of the ergodic hypothesis, see also comments in AppendixF below.

[4] 1868 seems to be the first time the hypothesis appeared: it has been again quite explicitly stated in [Boltzmann, 1871c]. It is well known that the strict interpretation of the hypothesis has been shown to be impossible: but the such an interpretation does not seem to have much in common with the work of the founding fathers, see below. Neither Boltzmann nor Maxwell employ here the words "ergodic hypothesis".

(c) Boltzmann goes back to the 1866 heat theorem and shows that the canonical distributions of a warm body, identified with the equilibrium states (as in 1866 were the periodic orbits), verify, in a quasi static process, the heat theorem, [Boltzmann, 1871d, #20]. *I.e.* it is possible to define entropy, specific heat *etc.* bound by the appropriate thermodynamic relations: this property will eventually be formalized as "thermodynamic analogy" or "thermodynamics model", see also comments in AppendixG below.

1872: Boltzmann's evolution equation is established greatly extending Maxwell's work where he had developed, in 1866 [Maxwell, 1866], a set of equations equivalent to Boltzmann's equation for the evolution of various key observables: it was a "weak version", to use modern, mathematical, language. The extension is a major conceptual advance, [Boltzmann, 1872, #22]. It was a manifestly irreversible equation and, via the H-theorem, allowed Boltzmann to develop a microscopic interpretation of equilibrium entropy (for rarefied gases) and to extend it to phenomena of evolution towards equilibrium. It ignited the discussion over microscopic reversibility versus macroscopic irreversibility, even though it did not lead to "other" advances with respect to Maxwell's work (aside, of course, entropy formula and H-theorem).

1877a: Boltzmann gives a first detailed analysis of the relation between microscopic reversibility and macroscopic irreversibility on observable time scales, [Boltzmann, 1877a, #39]. He also provides a more formal definition of thermodynamic analogy (the term is, however, not yet employed), with simple examples of the heat theorem in monocyclic systems, *i.e.* in systems in which all motions are periodic in phase space, see also comments in AppendixH below. Periodicity occurs in isolated systems with superastronomical periods, hence unobservable, but it is explained why irreversibility is nevertheless observable.

1877b: Detailed study, [Boltzmann, 1877b, #42], of phase space represented as a discretization on regular (parallelepipedal) cells. The count of configurations, somewhat extending the key 1868 work, leads Boltzmann to the well known expression of entropy, in equilibrium *as well as in systems approaching equilibrium*, as a measure of the "permutability" of the microscopic states. It achieves the identification of equilibrium configurations with the ones which are the most numerous among those which give the same values to a few observables of thermodynamic relevance (*i.e.* which realize the same "macrostate", [Lebowitz, 1993]). The *essential use of regularity of the discretization cells* does not seem to have been stressed enough by commentators, see also comments in AppendixI and Sec.8 below.

1881: Boltzmann, [Boltzmann, 1881, #63], presents Maxwell's analysis of his 1868 work, [Maxwell, 1879], attributing to Maxwell the ensembles view of the equilibrium statistics (as it is now called) and stressing that his own view (in the 1868 paper) rather considers the statistics defined by the frequency of visit to phase space regions. Maxwell's paper states clearly the ergodic hypothesis and does not mention that in [Boltzmann, 1871c, #19] Boltzmann had already

introduced and employed ensembles to describe equilibrium statistics (see AppendixF).

1884: Studies the Helmoltz' notion of thermodynamic analogy (which, without using this name, he already used in several earlier papers), [Boltzmann, 1884, #73]. The more formal set up leads Boltzmann to a general definition of the statistical ensembles as collections of "monodes", *i.e.* probability distributions on phase space invariant under time evolution, which are "orthodes", *i.e.* generate a thermodynamic analogy. The main examples that are described are: the "holode", the two parameters collection (temperature and volume) of canonical distributions, and the "ergode", the two parameters (energy and volume) collection of microcanonical distributions. The ensembles are connected via equivalence properties and the ergodic hypothesis implies that the microcanonical distributions describe the statistics controlling the physics of a system modeled by given Hamiltonian microscopic equations. In spite of the superastronomical (and unphysical) recurrence time, the hypothesis establishes the connection between physics and the thermodynamic analogies, see also comments in AppendixJ.

1971$\rightarrow \infty$: The "Sinai-Ruelle-Bowen", SRB, distributions are introduced to describe chaotic stationary states, [Ruelle, 1989, 1995]. Phase space discretized on a regular lattice and the ergodic hypothesis (hence periodic motions, still with superastronomical periods) reappear: will it be possible to develop a unified theory of equilibrium and stationary non equilibrium states? as well as of the approach to those? (see below).

2 Least action & periodicity: Boltzmann, Clausius.

In 1866 Boltzmann develops the idea that the second law simply reflects a very general property, actually a theorem, of Hamiltonian mechanics: under the ambitious title *On the mechanical meaning of the second fundamental theorem of heat theory*, [Boltzmann, 1866, #2].

After recalling that temperature should be identified as proportional to the time-average of kinetic energy, independent of the particular atom of the substance, (an already quite well known fact, *e.g.* see [Krönig, 1856, Maxwell, 1860]) Boltzmann tries to obtain a theorem "entirely coincident" with the form first discovered by Clausius, namely:

$$\int \frac{dQ}{T} \leq 0 \tag{1}$$

the integral being 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*", [Boltzmann, 1866, #2,p.24].

Boltzmann makes the point, in Sec.IV, that Eq.(1) is an extension of the least action principle: the latter compares very close motions which develop in a given time interval at *fixed initial and final positions*, concluding that if a motion satisfies Newton's equations then the variation of the action at it vanishes. The extension considered by Boltzmann compares instead very close *periodic motions* under the assumption that *both* satisfy Newton's equations: however technically the analytical procedure employed to perform the comparisons, *i.e.* the calculus of variations, is identical in the two cases, see p.34 below.

The basic assumption, [Boltzmann, 1866, #2,p.24], is that:

"*An arbitrarily selected atom moves, whatever is the state of the system, 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 speed and the direction come back to the original value in the same location, describing a closed curve and repeating, from this instant on, their motion. In this case the equality holds in* Eq.(1)."

In fact on the same page, Boltzmann mentions that, sometimes, motion might be not periodic: immediatey after stating the recurrence assumptions he comments that recurrence may occur "possily not exactly, nevertheless so similar ...".[5]

Notice that the above assumption only demands that each atom goes through a periodic orbit. The mathematical analysis is carried (see Sec.3 below for a version of the proof) in the case of a system consisting of a single atom or of a system of N atoms whose stationary motion is periodic in the $6N$ dimensional phase space. And it is extended to more general cases in which the motion can be quasi periodic involving many atoms each moving periodically (and, less formally, even more general).

It is remarkable that an analogous hypothesis, independently formulated, can be found in the successive paper [Clausius, 1871, l.8, p.438]: and indicates that, at the time, the idea of recurrence must have been quite common.

Clausius firstly imagines that the system consists of a single atom moving periodically; the proof is outlined in Sec.3 below (as in Boltzmann's work, it would apply to the case of an arbitrary system moving periodically on a path in the $6N$ dimensional phase space). [6] The position on the path is determined by the "phase", *i.e.* by the time, in units of the period, taken by the motion to

[5] And later in the paper, p.30, he acknowledges again that the motion might be aperiodic and develops an argument (rather involved) that, even so, it could possibly be regarded as periodic with infinite period,
"*"... this explanation is nothing more than the mathematical formulation of the statement according to which paths that do not close themselves in any finite time can be regarded as closed in an infinite time*". This seems to point at the remark that a stationary motion, confined in phase space, is generically bound to recur (as later formalized by Poincaré's recurrence theorem). An attempt to interpret this statement in a physical application is in [Gallavotti, 2014, I-6 & Appendix B] or [Gallavotti, 2000, Appendix 9.A3].

[6] However Clausius, and Boltzmann earlier, really discuss the motion of a single atom and choose not to stress that the proof would also work if the considered motion is that of the point representing the system in phase space.

return to its position and velocity from an arbitrarily fixed initial point; and at each time many phases are occupied (each by a different atom).

But Clausius, as already Boltzmann, is not strict about the recurrence. The assumption evolves eventually to one in which the atoms are supposed to be in different groups in which each atom follows a closed path but the period might depend on the group to which it belongs, and both authors go on to even more general cases (see Sec6 below).

Today any periodicity assumption, even in its evolved forms discussed in the following, is still often strongly criticized: social pressure induces to think that chaotic motions are non periodic and ubiquitous: and their images fill both scientific and popular magazines. It is however interesting and conceptually important that the ideas and methods developed or based on the primitive forms of periodic recurrence have laid the foundations of equilibrium statistical mechanics and have even been the basis of the chaotic conception of motion and of the possibility of reaching some understanding of it. *It will be argued below that periodicity can be a guide to the modern developments of nonequilibrium statistical mechanics.*

3 Heat theorem

The proofs of Boltzmann and Clausius can be read in the original papers, and compared; Clausius' version of the heat theorem is more general: for a comparison between the two proofs see Appendices A, B.

The analysis are based on what the Authors consider a version for periodic motions of the action principle in Maupertuis' form (at fixed extremes) $\delta \int \frac{m}{2} c ds = 0$ with c the speed and ds the arc length of the path followed by the motion x, rather than in the equivalent form $\delta \int_{t_1}^{t_2} (\frac{m}{2} c^2 - V(x)) \frac{dt}{t_2 - t_1} = 0$ (at fixed extremes in x and t). It will be summarized here following Clausius notations which are more clear, in the case in which the motion of the whole system is periodic.

If $t \to x(t)$ is a periodic motion developing with kinetic energy $K(x)$ and under the action of internal forces with potential energy $V(x)$ and of external forces with potential W,[7] then the average action of x is defined, if its period is τ, [8] by $\mathcal{A}(x) = \frac{1}{\tau} \int_0^\tau \left(\frac{m}{2} \dot{x}(t)^2 - V(x(t) - W(x(t))) \right) dt$.
We are interested in variations x' of x which are periodic: they will be repre-

[7] An example for a n points system $x = (q_1, \dots, q_n)$ enclosed in a container with boundary $\partial\Omega$ could be $V(x) = \sum_{i<j} v(q_i - q_j) + \sum_i v'(q_i)$, $W(x) = \sum_i w(d(q_i, \partial\Omega))$ with $w(r)$ a function of the distance $r = d(q, \partial\Omega)$ of q to $\partial\Omega$, steeply diverging at $r = 0$ (to model the container wall) and v, v' some potentials; if some part of $\partial\Omega$ is moved, as in a piston, the external potential changes by $\delta_e W$; of course if Ω is fixed W can be thought as included in V.

[8] The original notation of Clausius for the period was i, which today might seem unusual, while for Boltzmann was $t_2 - t_1$: here the period will be denoted τ, for simplicity

sented as

$$x'(t) = x'(\tau'\varphi) \stackrel{def}{=} \xi'(\varphi), \quad t \in [0, \tau'],$$
$$x(t) = x(\tau\varphi) \stackrel{def}{=} \xi(\varphi), \quad t \in [0, \tau],$$
$$\delta\tau = \tau' - \tau$$

where i', i are the periods, and ξ', ξ are periodic functions in $\varphi \in [0, 1]$; the φ is the *phase*, as introduced in [Clausius, 1871], and corresponds to the variable called *average anomaly* in astronomy, see Fig.1.

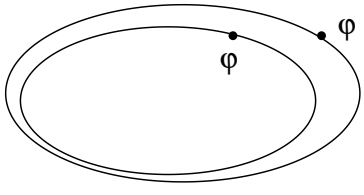

fig.1

.

Fig.1: A periodic path and another one close to it: the paths can be imagined to be two curves in phase space of equations $\varphi \to \xi(\varphi)$ or $\varphi \to \xi'(\varphi)$ periodic in $\varphi \in [0, 1]$; if the periods of the two motions are i and i' the position at time t of each will be $\xi(\frac{t}{\tau})$ or $\xi'(\frac{t}{\tau'})$. Hence Clausius' phases correspond to the astronomical average anomalies.

The role of φ is simply to establish a correspondence between points on the initial trajectory x and on the varied one x': it is manifestly an arbitrarily chosen correspondence, which could be defined differently without affecting the final result, but convenient in order to follow the algebraic steps. It should be noted that in [Boltzmann, 1866, #2] the phase is not introduced and this makes the computations difficult to follow.[9]

The two motions to be compared have to be thought as characterizing the system state at two successive steps of a reversible process: the duration of each step of the process is very long, enough to cover many full periods so that each observable has acquired a well defined new average value.

Set $\overline{F}(x) = \tau^{-1} \int_0^\tau F(x(t))dt = \int_0^1 F(\xi(\varphi))\, d\varphi$ for a generic observable $F(x(t))$; for instance F could be the difference between kinetic energy and potential energy $\mathcal{A}(x(t)) = K(x(t)) - V(x(t) - W(x(t)))$ and its average would be the average action $\overline{\mathcal{A}}(x)$.

Then the new form of the "action principle for periodic motions" is, calling $\delta_e W$ the variation of external potential (with no loss of generality $W = 0$ could be supposed to hold at the beginning of the process considerably simplifying the following formulae)

$$\delta\overline{\mathcal{A}} \stackrel{def}{=} \delta\overline{K - V - W} = -2\overline{K}\delta\log\tau + \delta_e\overline{W} \qquad (*)$$

allowing here *also* for a variation $\delta_e W$ of the potential of the external forces (think of a volume change and of the work by the pressure) driving the new motion x' of period τ' (which is itself a variation of the motion x of period

[9] In the sense that once realized which is the final result, it is easier to reproduce it rather than to follow his calculations.

τ): Eq.(*) yields the correction to the expression $\delta\overline{\mathcal{A}} = \delta\overline{K - V - W} = 0$ for the variation at *fixed* temporal extremes and fixed potentials, familiar from the action principle.[10]

In deriving Eq.(*), which is the authors' common conclusion, there is *no stationarity condition* to consider: it holds if and only if the variation changes a periodic motion x into a nearby periodic one x' developing under forces varied by the variation $\delta_e W$ of the external forces potential, as it is imagined in the theory considered (*but in Boltzmann it is supposed* $\delta_e W = 0$, see below). Furthermore *the variation is not arbitrary* (unlike the case of the usual least action principle) but occurs between given motions which are both periodic solutions of the corresponding equations of motion.

The connection with the heat theorem derives from the remark that in the infinitesimal variation of the orbit from x to x' its new total energy is $\overline{U}' \stackrel{def}{=} \overline{K}' + \overline{V}' + \overline{W'}$ and changes from the old $\overline{K} + \overline{V} + \overline{W}$ by $\delta\overline{K + V + W}$).

Since $\delta_e\overline{W}$ is interpreted as the external work the quantity $\delta Q \stackrel{def}{=} \delta\overline{U} - \delta_e\overline{W} \equiv \delta(\overline{K} + \overline{V} + \overline{W})$ is interpreted as the heat δQ received by the system and the variational relation (*) above can be rewritten:

$$\begin{aligned} &-\delta Q + 2\delta\overline{K} + 2\overline{K}\delta\log\tau \equiv -\delta Q + 2\overline{K}\delta\log(\overline{K}\tau) = 0 \\ &\Rightarrow \quad \frac{\delta Q}{\overline{K}} = 2\delta\log(\overline{K}\,\tau) \end{aligned} \qquad (**)$$

with the last = signs holding if the system can be considered to satisfy the equations of motion during the transformation, which means if the variation δ is "quasi static". Hence in a quasi static transformation $\overline{K}^{-1}$ is an integrating factor for δQ: and the primitive function (*i.e.* the entropy) is twice the logarithm of the ordinary action $S = 2\log\tau\overline{K}$, up to an additive constant.

About Eq.(*) Boltzmann says:

"*It is easily seen that our conclusion on the meaning of the quantities that intervene here is totally independent from the theory of heat, and therefore the second fundamental theorem is related to a theorem of pure mechanics to which it corresponds just as the kinetic energy principle corresponds to the first principle; and, as it immediately follows from our considerations, it is related to the least action principle, in a somewhat generalized form.*", [Boltzmann, 1866, #2,sec.IV]

[10] To derive Eq.(*) represent a periodic motion of period i as $x(t) = \xi(\varphi)$, with $t = \tau\varphi$ and $\varphi \to \xi(\varphi)$ periodic with period 1; and, likewise, represent a close motion with period τ' as $x'(t) = \xi(\varphi) + \eta(\varphi)$ with $t = \tau'\varphi$: computing to first order the $\frac{1}{\tau'}\int_0^{\tau'} dt(\frac{m}{2}\dot{x}'(t)^2 - V(x'(t)) - W(x'(t)) - \delta_e W(x'(t)))$ and *applying the equations of motion* for a motion x developing under the influence of a force with potential $V + W$, or for x' developing under a potential $V + W + \delta_e W$: $\ddot{x}'(t) = -\partial_x(V(x'(t) + W(x'(t)) + \delta_e W(x'(t))))$ in the process changing x into x'.
Remark that if $\delta Q = 0, \delta_e W = 0$ Eq.(*) becomes $\delta(\tau\overline{K}) = 0$, *i.e.* $\delta\int_0^\tau K dt = 2\delta\oint cds$ which can be seen as a periodic version of the least action principle applied to either the initial motion or to the varied motion.

Both Boltzmann and Clausius call Eq.(*) a "generalization of the action principle": it should be noted that the latter principle uniquely determines a motion, *i.e.* it determines its equations; Eq.(*), instead, does not determine a motion but it only establishes a relation between the variation of average kinetic and potential energies of close periodic motions under the assumption that they satisfy the equations of motion; and it does not establish a variational property.

Also Eq.(*) does not establish the general inequality $\oint \frac{dQ}{T} \leq 0$: which in Boltzmann is obtained via a further argument at the end of the paper, while Clausius does not even mention the inequality, *leaving it, implicitly and to the reader, as consequence* of having allowed in his formulation variable external forces (*i.e.* $\delta_e W \neq 0$) so that the result applies to a general cycle in which heat and work are involved: remarkably his paper contains *no signs* $\geq$ *or* $\leq$*, but only equalities* ! [11]

In the case in which the motion of the atoms is not periodic in phase space and the atoms can be divided in groups with different periods the heat theorem can be extended: both Boltzmann and Clausius, in modern notations, say the following. Let the internal interaction potential be $V(x) = \frac{1}{2}\sum_{r\neq s} V(x_r - x_s)$ and suppose that particle s moves with period i_s: then the variational analysis leading to Eq.(*) above yields (for simplicity take $W = 0$ in the first motion)

$$\delta(\overline{K}_r - \frac{1}{2}\sum_{s\neq r}\overline{V}(x_r - x_s)) = -2\overline{K}_r\delta\log\tau_r + \delta_e\overline{W}_r$$

hence, as above,

$$\delta Q_s \stackrel{def}{=} \delta(\overline{K}_s + \frac{1}{2}\sum_{s\neq r}\overline{V}(x_r - x_s)) = 2\overline{K}_s + 2\overline{K}_s\delta\log\tau_s, \qquad \text{summing :}$$

$$\delta Q = \sum_s \delta Q_s = \delta(\overline{K} + \overline{V}) = \sum_s (2\delta\overline{K}_s + 2\overline{K}_s\delta\log\tau_s)$$

and *since* $\overline{K}_s$ *is* s*-independent* by the earlier equipartition result (of Maxwell) this shows that $\frac{\delta Q}{\overline{K}}$ is exact.

Hence if there are several periods, so that the motion is quasi periodic, the heat theorem still holds (because in the quasi static process the time that elapses in an infinitesimal step of a process is "quasi infinite" so that all averages are reached). However the simplest assumption is to suppose that the motion is periodic in phase space: which *appropriately formulated* will become the ergodic hypothesis.

[11] This is an important point: Eq.(**) does not give to the periodic orbits describing the state of the system any variational property (of minimum or maximum): the consequence is that it does not imply $\oint \frac{\delta Q}{T} \leq 0$ in the general case of a cycle but only $\oint \frac{\delta Q}{T} = 0$ in the (considered) cases of reversible cycles. In Clausius' derivation, thanks to the inclusion of extrenal forces, the equality proves existence of entropy, therefore, by earlier classical arguments (again due to Clausius), also the inequality follows for non reversible cycles.

4 An example

It is instructive to illustrate via a simple explicit example, the construction of the function S. The example in the form below is extracted from the later work [Boltzmann, 1877a, #39,p.127-148]. It explains why and how a concept that will play an important role in the development of the theory of the ensembles, namely the "thermodynamic analogy"[12] or "model of thermodynamics" already arises in very simple systems in which a general analysis can be performed.

The example is built on a case in which all motions are really periodic, namely a one-dimensional system with potential $\varphi(x)$ such that $|\varphi'(x)| > 0$ for $|x| > 0$, $\varphi''(0) > 0$ and $\varphi(x) \xrightarrow[x\to\infty]{} +\infty$. All motions are periodic (systems with this property are called *monocyclic*, [Boltzmann, 1884, #73],[Gallavotti, 2014, p.205],[Gallavotti, 2000, p.45]. Suppose that the potential $\varphi(x)$ depends on a parameter V, thus denote it φ_V.

Define *a state* to be a motion with given energy U and given V (*i.e.* a periodic motion). And call:

U = total energy of the system $\equiv K + \varphi$
T = time average of the kinetic energy K
V = the parameter on which φ is supposed to depend
p = $-$ average of $\partial_V \varphi$.

A state (*i.e.* a periodic motion) is therefore parameterized by U, V and if such parameters change by dU, dV, respectively, let

$$dW = -pdV, \qquad dQ = dU + pdV, \qquad \overline{K} = T.$$

Then, if $i = i(U, V)$ is the period, the heat theorem is, in this case, [Boltzmann, 1868b, #6], [Boltzmann, 1877a, #39],[Helmholtz, 1895b]: :

Theorem The differential $(dU + pdV)/T$ *is exact and equal to the differential of "entropy"* $S \overset{def}{=} 2\log(iT)$*, see Eq.(**) Sec.3.*

In fact let $x_\pm(U, V)$ be the extremes of the oscillations of the motion with given U, V and define S as:

$$S = 2\log 2 \int_{x_-(U,V)}^{x_+(U,V)} \sqrt{K(x; U, V)}dx = 2\log \int_{x_-(U,V)}^{x_+(U,V)} 2\sqrt{U - \varphi(x)}dx$$

so that $dS = \frac{\int \left(dU - \partial_V \varphi(x) dV\right) \frac{dx}{\sqrt{K}}}{\int K \frac{dx}{\sqrt{K}}} \equiv \frac{dQ}{T}$, and $S = 2\log i\overline{K}$ if $\frac{dx}{\sqrt{K}} = \sqrt{\frac{2}{m}}dt$ is used to express the period i and the time averages via integrations with respect to $\frac{dx}{\sqrt{K}}$.

Therefore Eq.(**) of Sec.3 is checked in this case. This completes the discussion of the case in which motions are periodic. For an interpretation of the above proof in a general monocyclic system see [Boltzmann, 1884, #73].

[12] Original Boltzmann's term.

The case of Keplerian motions, actually treated in [Boltzmann, 1877a, #39], is more delicate and interesting because all confined motions are periodic but there is an extra constant of motion, [Boltzmann, 1884, #73],[Gallavotti, 2000, p.45] and [Gallavotti, 2014, Appendix D].

5 Boltzmann vs. Clausius: on priority

Since both Boltzmann and Clausius reach a similar conclusion a priority discussion arose leading to a detailed comparison of the two works. Boltzmann started with:

"*.... I believe I can assert that the fourth Section of my paper published four years earlier is, in large part, identical to the quoted publication of Mr. Clausius. Apparently, therefore, my work is entirely ignored,...*", [Boltzmann, 1871a, #17].

Clausius reacted politely but firmly. He objected to Boltzmann the obscurity of his derivation obliging the reader to interpret suitably formulae that in reality might be not explained (and ambiguous), [Clausius, 1872, p.267]:

"*... the first of these Boltzmann's equations will be identical to my Eq.(I), if the value assigned to ε can be that of my equation.*"

but the values of ε, according to Clausius, could not be compared because of the different definition of averages and variations.

Such first difference between the two works, as Clausius points out, is due to some ambiguity in the definition of the averages because it is not clear which is the correspondence, between the times in the motion x and in the varied motion $x + \delta x$, that should be considered in comparing the averages; Clausius is very careful about this point and he says that, because of this difference, the two variations appearing in the definition of ε above cannot be really compared without a proper interpretation of the symbols.[13]

The main difference, however, is that in Boltzmann's discussion the motions whose actions are compared are imagined as end products of an infinitesimal step of a quasi static thermodynamic process in which *the external potential does not change*: therefore the class of transformations to which the result applies is very restricted, *e.g.* in the case of a gas it would restrict the theory to the isovolumic transformations, as stressed by Clausius, see AppendixB: who points out that this is a key difference between his analysis and Boltzmann's which otherwise would be equivalent.

Boltzmann had realized the point, and admitted it, already in his priority claim paper: while promising to take variable external potential into account in his later works, he had also written that disregarding the external potential variability had been a choice done to simplify the argument since inclusion of

[13] Actually the correspondence is mentioned quite explicitly in the formulation of the action principle in [Boltzmann, 1866, #2,p.32].

external potential variations would have been easy without affecting his deduction.

After Clausius reply (and strong disagreement) he did not insist on the matter and did not profit from the fact that his formulae remain the same, under further interpretations, even if the external potential changes; this was concluded by Clausius himself at the end of his exegesis of Boltzmann's work, see p.39 below, by the sentence "*... but I want to stress that such solution appears well simpler when it is found than when it is searched*".

Still Boltzmann did really deal with the promise about taking into account the external forces in the same year, [Boltzmann, 1871d, #20], in great detail and adopting a new viewpoint in which periodic motion, as a representative of a state, was replaced by stationary probability distributions, considering in particular the cases of the canonical and microcanonical distributions (and referring (on p.302 of [Boltzmann, 1871d]) to the connection with his old work without mentioning again Clausius): and developed key examples of what later would be called *thermodynamic analogy*.

It should also be said that Boltzmann's analysis, even if restricted to the simpler completely periodic case, is quite difficult to follow: but as Clausius says, if interpreted correctly, it is right; on the other hand Clausius' is very clear (at least when treating the same case).

Of course with Boltzmann remains, besides the proposal of a relation between the microscopic Hamiltonian laws of motion and the second law of (equilibrium) thermodynamics, the "novel idea" that the states of the system are to be identified with the average values of physical quantities computed on a (periodic) trajectory thus building, at least, a "thermodynamic analogy", see Sec.10 below: the 1866 work is an early stage of the developing concept of state as a stationary distribution. An equilibrium state is identified with the average values that the observables have in it: in the language of modern measure theory this is a special probability distribution, with the property of being invariant under time evolution.

It should finally be kept in mind that, by the time Clausius' work appeared, and Boltzmann was upset, Boltzmann had gone *far beyond* his work of 1866, see also AppendixC below: but the priority claim discussion dealt solely with the subject of the two papers on the least action principle which were, in a sense, *already quite outdated* with respect to the early breakthrough work [Boltzmann, 1866, #2], mainly because of the new major breakthrough by Boltzmann himself in [Boltzmann, 1868a, #5].

For more detailed comments see AppendicesA,B below.

6 On periodicity

Both Boltzmann and Clausius were not completely comfortable with the periodicity of atomic motions.

In Sec.3 Boltzmann has been quoted as assuming periodicity and then saying that strict periodicity is not necessary and even presented an elaborate argument

to conclude that, at least for his purposes, in the cases in which the paths did not close nevertheless they could be "*considered closed in an infinite time*", see p.6 above.

Clausius worries about such a restriction more than Boltzmann does; he is led to think the system as consisting of many groups of points which closely follow an essentially periodic motion, [Clausius, 1871, Sec.13,p.452]:

"*..temporarily, for the sake of simplicity we shall assume, as already before, that all points describe closed trajectories. For all considered points, that move in a similar manner, we suppose, more specifically, that they go through equal paths with equal period, although other points may run through other paths with other periods. If the initial stationary motion is changed into another, hence on a different path and with different period, nevertheless these will be still closed paths each run through by a large number of points.*"

each atom or small group of atoms undergoes a periodic motion and the statistical uniformity follows from the large number of evolving units. [14]

Then he dedicates the entire last three sections (13–15) of his work to weakening further the periodicity assumption:

"... In the present work we have supposed until now that all points move on closed paths. We now want to set aside also this assumption and concentrate on the hypothesis that the motion is stationary.
For motions that do not run over closed trajectories the notion of recurrence is no longer usable in a literal sense, therefore it is necessary to talk about them in another sense. Consider therefore right away motions that have a given component in a given direction, for instance the x direction in our coordinates system. It is then clear that motions go back and forth alternatively, and also for their elongation, speed and return time, as it is proper for stationary motion, the same form of motion is realized. The time interval within which each group of points which, approximately, behave in the same way admits an average value."

without assuming the *one dimensional* motions of the three coordinates separately periodic with the same period (which would mean that the motions are periodic) he supposes "only" that the variation δi of the periods are the same for the three coordinates when the motions of the particles are varied. The particles can be collected into groups with the same δi and the same kinetic energy:

To proceed further to treat such equations a difficulty arises because the velocity v, as well as the return time interval i, may be different from group to group ...

an argument follows to justify that the *average* $\overline{v^2}$ can be regarded at each step

[14] The assumption can be seen as an assumption that all motions are quasi periodic and that the system is integrable: it is a view that *mutatis mutandis* resisted until recent times both in celestial mechanics, in spite of Poincaré's work, and in turbulence theory as in the first few editions of Landau-Lifschitz' treatise on fluid mechanics, [Landau and Lifschitz, 1971].

of a quasi static process as constant in a stationary state[15] for all groups of particles and concludes that the analysis leading to Eq.(**), in Sec.3 above, can be repeated and the entropy variation can be expressed as proportional to $\sum \delta \log(Ti)$ (with T a constant proportional to the average kinetic energy but with i possibly variable, from group to group and particle to particle appearing in the sum).

Summarizing, a simplified picture is: particles move periodically and can be collected in groups with the same average kinetic energy T per particle, whose equipartition is implied by stationarity, and $\frac{\delta Q}{T}$ is exact and the entropy is proportional to $\sum \log(Ti)$, where the sum runs over the different particles: *i.e.* the variation of the entropy is the sum of the variations of the entropies of each group.

Finally it should be mentioned, as I argue explicitly in Sec.8,9 below, that it cannot be said, that Boltzmann abandoned the periodic orbits and the related Ergodic Hypothesis to switch to the theory of ensembles.

7 Ergodic hypothesis: Boltzmann & Maxwell

The work [Boltzmann, 1868a, #5]:[16] is remarkable because in it Boltzmann derives the probability distribution, today called *microcanonical*, for the phase space points that represent an entire "warm body". But the key assumption in the derivation is not proposed explicitly and has to be extracted from the text because, although used, it is not mentioned as such. It was later recognized and most vividly commented in [Maxwell, 1879, p.734], as:

" *The only assumption which is necessary for the direct proof* [of the microcanonical distribution by Boltzmann] *is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy. Now it is manifest that there are cases in which this does not take place*

...

But if we suppose that the material particles, or some of them, occasionally encounter a fixed obstacle such as the sides of a vessel containing the particles, then, except for special forms of the surface of this obstacle, each encounter will introduce a disturbance into the motion of the system, so that it will pass from one undisturbed path into another...."

[15] This is because each periodic motion is supposed run by a large number of particles of a given group with different phases and the independence (*i.e.* equipartition), from the group itself, of the average kinetic energy of the motions in each group is due to the stationarity of the state of the system.

[16] Initially motivated to reproduce Maxwell's result "*because the exposition of Maxwell in its broad lines is difficult to understand*". The strong assumption, set at the beginning, of restricting the result to the case of a very rarefied gas (to neglect the time of interaction versus the time of free flight of an atom) is, later in the paper, removed and periodicity can be imagined to have been *implicitly* reintroduced, see Maxwell comment below, through the identification between probabilities and frequencies of visits.

It might take a long time to do the travel but eventually it will be repeated.[17] Maxwell interprets Boltzmann without invoking external random actions, and if intepreted in this way (see the full quote of Maxwell below, p.49) this is essentially the *Ergodic Hypothesis*, see below.

In [Boltzmann, 1868a, #5], besides a new proof of Maxwell's distribution, the microcanonical distribution (so called since Gibbs) is obtained not only without explicit reference to periodicity but, partitioning phase space into cells, via the combinatorial count of the number of ways to divide energy (just kinetic in Sec.II and total in Sec.III of [Boltzmann, 1868a, #5]) into a sum of energies, keeping the total sum fixed.

The combinatorial argument in Sec.II, dealing with the case of a rarefied system, in which the interaction time can be neglected so that kinetic energy can be considered constant, and aiming at obtaining Maxwell's velocity distribution, supposes that each among the discrete kinetic energy values probability is proportional to the time spent by the system in the cell. After checking that the *velocity space* volume element remains the same at every pair collision this is done by inserting in the energy levels one particle at a time and counting how many possibilities one has at each time: this will be the number of different microscopic configurations with a given total kinetic energy: it can be identified with their probability if the different microscopic configurations are cyclically permuted by the time evolution as it becomes more clear in Sec.III.

The argument is extended in Sec.III to cover the case of *non negligible time of interaction between the particles*. The phase space volume elements conservation is checked *without assuming only pair collisions* (an assumption impossible in presence of non negligible range of interaction) and in the full phase space[18] The kinetic energy of the n-particles configurations with the $3n$-position coordinates

[17] Here Maxwell refers to the proof of the microcanonical distribution in [Boltzmann, 1868a, #5], where it had been derived after releasing, in Sec.II,III, the strong assumption made in Sec.I, of a very rarefied gas (to neglect the time of interaction versus the time of free flight of an atom). In the paper the probability is identified and defined as proportional to the time of visit to small rectangular cells filling the entire available phase space: and this is simply realized if the phase space point representing the microscopic configurations visits all the discrete cells (since the cells may contain several particles one cannot really imagine other possibilities if the size of the cells is left arbitrary, so Maxwell's interpretation seems the only possible once a discrete phase space is accepted). Maxwell's remark is interesting as it formulates again the hypothesis in [Boltzmann, 1868a, 1871c] in the strong form which, if interpreted as several critics did, would be mathematically incorrect. In [Inaba, 2015] is analyzed the importance of this work of Maxwell for the foundations of the theory of the ensembles as representing a single invariant distribution on phase space via a collection of independent copies of the same system.

[18] This follows via the by now usual argument employed to prove Liouville's theorem, [Boltzmann, 1868a, #5,p.93-95], 1868. It will be again proved later in [Boltzmann, 1871b, #18]. It is unclear why Maxwell, in commenting the latter work in [Maxwell, 1879], while attributing to Boltzmann the theorem, develops a proof quite close to the one in [Boltzmann, 1871b, #18] but refers to the 1868 paper only. Also unclear is why neither author refers to Liouville's theorem of 1838, while proving it over and over again and still in 1881, [Boltzmann, 1868a,b, 1871c, 1877b, 1872, Maxwell, 1879, Boltzmann, 1881], so that one has to conclude that the theorem was not well known, yet, at the date. It should also be stressed that nowhere the authors mention that the volume elements are deformed by the evolution, so that it has to be imagined that they are really thought as points, see Sec.8,9 below.

$q = (q_1, \ldots, q_n)$ in a given position space cell is $n\kappa - \chi(q)$, if $\chi(q)$ is potential energy, is partitioned in all possible ways among the kinetic energy levels. The microcanonical distribution is obtained by essentially the same combinatorial argument of Sec.II but using also a discretization of positions: thus assuming that the phase space trajectory visits all cells in the *available* phase space, as pointed out by Maxwell.[19]

The above mentioned hypothesis may seem stronger than the ergodic hypothesis because it deals with phase space and does not mention the exceptions that are allowed in the mathematical version of the hypothesis: but it deals with motion discretized in finitely many cells and therefore it is simply different from the mathematical version, and the usual impossibility argument cannot be used.[20]

The periodicity property remains in the background and the possibility arises that it could even be forgotten and replaced by a direct assumption that the probability of configurations in phase space is simply obtained by counting the number of ways of realizing them in phase space. This may seem (a new assumption and) an easy way out of the unphysically long time scales in which periodicity would become manifest.

But Boltzmann always identified probabilities with visits frequencies and did not really abandon the periodic conception of the systems motions: eventually developed arguments to show that periodicity plaid the "role of a symmetry property" which implied, for very small or very large systems, properties that become observable in "human time scales", as predicted by Boltzmann's equation for dilute gases in [Boltzmann, 1872, #22], for the deep reason that they hold for *most* system configurations, [Boltzmann, 1877a, #39] and [Boltzmann, 1884, #73].

8 Discrete phase space, ergodicity & regular cells.

The hypothesis that the statistics of the equilibrium states are given by probability distributions over all states compatible with energy conservation, through which the phase space point representing the state cycles periodically, had been used in the 1868 work of Boltzmann, as recognized by Maxwell, see Sec.7 above and Appendix C below. It has to be properly interpreted and it is the "Ergodic Hypothesis".

[19] The result is given only after integrating it over the velocities, [Boltzmann, 1868a, #5,p.95,l.-6]: for details see Appendix C.

[20] From a mathematical point of view it is obviously impossible that a periodic trajectory covers entirely a region of space and the assumption needs intepretation (because, out of respect for the founding fathers, it cannot be just dimissed). For instance, if the forces are supposed smooth, consider a point in a small enough volume Δ in phase space: the velocity (of the phase space point representing the system configuration) will be non zero and data initially in Δ will go out of it without being able to return before a time τ necessarily positive and independent of the initial location within Δ. Therefore the initial point can return to Δ only finitely many times during the period if its motion; each time it will cover a smooth segment in Δ; but a finite number of smooth segments cannot cover the continuum of points in Δ.

It is important *not* to identify this with the similar statement mentioned by Boltzmann around 1870 for the molecules in a rarefied gas, see p.237,l.8, in [Boltzmann, 1871b, #18], about the internal motion of atoms in single molecules of a gas: "*it is clear that the various gas molecules will go through all possible states of motion*". This property is attributed as due to collisions between different molecules: viewed as non periodic, stochastic, events which make the state of a single molecule assume all the possible configurations (on a time scale far shorter than any global recurrence). As shown in the same key work [Boltzmann, 1871b], the latter property implies the canonical distribution for the molecules states, while the ergodic hypothesis implies the microcanonical distribution for the whole "warm body".

Boltzmann, shortly afterwards and closer to Maxwell's interpretation (Sec.7 above, quoted in full in AppendixC, p.49 below) of the hypothesis of his own 1868 paper, gives a more precise formulation, [Boltzmann, 1871c, #19,p.284] (see also AppendixF below):,

*Finally from the equations derived above we can, under an assumption which it does not seem to me of unlikely application to a warm body, directly access to the thermal equilibrium of a polyatomic molecule, and more generally of a given molecule interacting with a mass of gas. The great chaoticity of the thermal motion and the variability of the force that the body feels from the outside makes it probable that the atoms [*of the molecules*] take in the motion, that we call heat, all possible positions and velocities compatible with the equation of the kinetic energy [*conservation of energy*], and even that the atoms of a warm body can take all positions and velocities compatible with the last equations considered.*[21]

The last sentence here has to be particularly remarked as it jumps from the properties of *atoms inside molecules* immersed in a gas to properties of *atoms in a warm body* as demanded by the ergodic hypothesis.

In the [Boltzmann, 1868a, #5] work the assumption is used to imply that since the motion visits the whole phase space then the frequencies of visit to regions must be described by a density function which must be invariant under time evolution (because of the phase space volume conservation), leading to the microcanonical distribution for the whole system, see [Boltzmann, 1868a, #5,p.95,l.-6], and to a canonical distribution for the individual molecules.

The view that the equilibrium distribution should be representable by a density on phase space which ought to be > 0 for all configurations compatible with energy conservation did not really demand the intervention of random

[21] The "variability of the force that the body feels from the outside" and molecular collisions appear essential for the statement to hold for the atoms of a single molecule, see also [Brush, 2003]: however the variability *should not* be intended as "random" when stating "...even that the atoms of a warm body ...". In [Maxwell, 1879] this "variability" is exemplified by referring to the roughness (and not the randomness) of the interactions with a container: so the statement is still about deterministic, time independent, interactions. Only in cases in which the system admits constants of motion due to symmetries that are not generic, the system may avoid visiting all possible positions and velocities compatible with the equation of the kinetic energy, [Boltzmann, 1868a, #5,p.96], see also the comment in the recent collection [Boltzmann, 2000, p.xxviii]..

external forces. This is made clear by the immediately following work, [Boltzmann, 1868b, #6], where an example is discussed in detail: however 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, see comments in AppendixC,D below.[22]

His later works, starting with [Boltzmann, 1871b, #18], show that he later realized this possibility and was very concerned about it: density 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 have to be added as supporting assumptions.

Most important, in the three 1871 papers [Boltzmann, 1871b,c,d], as already in the earlier [Boltzmann, 1868a, #5] work, equipartition may appear as obtained without using the equations of motion, except for the pair collisions conservation laws or via a discrete representation of the states of the atoms, classified through discrete values of their possible kinetic energy and positions, determined by a partition of all the available phase space into parallelepipedal cells (as in the above quoted hypothesis).[23] This allowed to set up the determination of the probability of the states (as points in phase space) via a combinatorial argument.

Nevertheless dynamics is deeply linked to the derivations because the probability of finding a microscopic configuration is *identified with the fraction of time, in its evolution, it spends inside a given cell* and is implied by the assumption that the phase space point representing the system visits cyclically all *discrete cells* into which phase space is divided. And this is the complete *interpretation of the Ergodic Hypothesis* (distinct from its modern interpretation in the ergodic theory of dynamical systems).

Discretization of phase space into cells is done systematically in [Boltzmann, 1877b, #42] going well beyond the [Boltzmann, 1868a, #5], in the sense that the program of computing probabilities by counting the number of ways of realizing the microscopic configurations in a discretized phase space is presented as a general method and used to provide strength to the analysis in the earlier paper on Loschmidt's irreversibility question, where the "sea of Boltzmann" (as Uhlenbeck,[Uhlenbeck, 1968], called it) was introduced, [Boltzmann, 1877a, #39], see AppendicesH,I.

It should be noted and stressed that in the discretisation used the phase space cells are parallelepipeds:[24] *this is an essential point not really stressed in*

[22] By other constants of motion one should understand smooth constants. Boltzmann did not really consider functions which are not smooth (*i.e.* just measurable) and which are essential in modern mathematical problems in ergodic theory.

[23] The initial restriction that the density be so low that the time of free flight be overwhelmingly large compared to the collision time *is lifted* in Sec.III of [Boltzmann, 1868a, #5].

[24] Cubes in space times cubes in momentum. At least this is so in [Boltzmann, 1877b, #42]: while in [Boltzmann, 1868a, #5] the cells in momentum space were simply cells in which energy $\frac{1}{2}mc^2$ was between e and $e+de$, with $de=\frac{1}{p}$ (p very large) and had a multiplicity proportional to $\sqrt{e}de$ in 3-dimensional space, which is appropriate for *cubic cells* of side $\frac{1}{p}$.

the literature. Boltzmann does not comment on that: but he wants to think, as he repeatedly wrote since realizing that his ideas were misunderstood, that derivatives and integrals are just "approximations" of certain ratios and sums, [Dugas, 1959, p.25-29].

This means, if ratios and sums are to be interpreted as the usual derivatives and integrals, that the discretization of phase space and time must be done via a regular lattice.

The laws of nature can be formulated *via discrete difference equations or equivalently by the usual corresponding differential equations* only if the discretization is imagined on a *regular lattice*, *e.g.* a parallelepipedal one (the parallelepipeds being $3N$ dimensional cubes in positions space times $3N$ dimensional cubes in momentum space). If discretizations were performed on discrete approximations of fractals, *i.e.* irregular (even though scaling symmetric) sets of points, currently considered in various fields, the laws of nature would be very different (maybe needing fractional derivatives in their continuum versions) and the Gibbs distributions, for instance, could be quite different.

This becomes a key point in the modern approaches to nonequilibrium in which the analogue, for instance, of the microcanonical distribution in general dissipative systems is determined,[25] and in the conceptual unification between equilibrium and nonequilibrium, see [Gallavotti, 2014].

9 Boltzmann on discreteness

The discrete view of phase space makes it mathematically possible to say that a point visits all phase space cells: but this statement was attributed to Boltzmann and criticized over and over again (see [Brush, 2003, p.505]) even by Physicists, including in the influential book, [Ehrenfest and Ehrenfest, 1990], although enlightened mathematicians could see better, see p.385 in [Brush, 1976]).

Therefore the question: *can it be said that the not mathematically formalized ergodic hypothesis of Boltzmann, Clausius and Maxwell by chance led them to statistical mechanics*, just on the grounds that its mathematical interpretation "cannot be true" as proved in several Mathematics and Physics works? should be answered simply "no". But not simply because formalizing a statement into one that via Mathematics can be proved right or wrong is ambiguous.[26]

The point is that for Boltzmann, for instance, phase space was discrete and points in phase space had finite size, that I will call h^3 as customary, and were located on a *regular lattice*. And time evolution was a permutation of them: ergodicity meant therefore that the permutation was just a *one cycle permutation*. This is very cearly discussed by Dugas in [Dugas, 1959, p.25-29], as followed here.

[25] This is the SRB distribution, [Ruelle, 1989].

[26] Many famous results in Mathematics became correct after the very formulations of the problems originating them was slightly changed, as the KAM theorem story reminds.

It does not seem that in the original viewpoint Boltzmann's systems of particles were really thought of as susceptible of assuming a $6N$ *dimensional continuum of states.*

The relation between the apparent continuum of reality, as we perceive it and input it in most of our models or theories for its interpretation and understanding, and the possibly intrinsic and deep discrete nature of reality and/or of our own thinking is exemplified explicitly in many among Boltzmann's writings, for instance, [Boltzmann, 1974, p.169]:

Therefore if we wish to get a picture of the continuum in words, we first have to imagine a large, but finite number of particles with certain properties and investigate the behavior of the ensemble of such particles. Certain properties of the ensemble may approach a definite limit as we allow the number of particles ever more to increase and their size ever more to decrease. Of these properties one can then assert that they apply to a continuum, and in my opinion this is the only non-contradictory definition of a continuum with certain properties

Or also, [Boltzmann, 1974, p.56].:

"*The concepts of differential and integral calculus separated from any atomistic idea are truly metaphysical, if by this we mean, following an appropriate definition of Mach, that we have forgotten how we acquired them*"

And, [Boltzmann, 1974, p.55]:

"*Through the symbols manipulations of integral calculus, which have become common practice, one can temporarily forget the need to start from a finite number of elements, that is at the basis of the creation of the concept, but one cannot avoid it*".

or, [Boltzmann, 1974, p.227]:

"*Differential equations require, just as atomism does, an initial idea of a large finite number of numerical values and points ..... Only afterwards it is maintained that the picture never represents phenomena exactly but merely approximates them more and more the greater the number of these points and the smaller the distance between them. Yet here again it seems to me that so far we cannot exclude the possibility that for a certain very large number of points the picture will best represent phenomena and that for greater numbers it will become again less accurate, so that atoms do exist in large but finite number*

and, [Boltzmann, 1974, p.55-56]:

"*This naturally does not exclude that, after we got used once and for all to the abstraction of the volume elements and of the other symbols* [of calculus] *and once one has studied the way to operate with them, it could look handy and luring, in deriving certain formulae that Volkmann calls formulae for the coarse phenomena, to forget completely the atomistic significance of such abstractions.*

They provide a general model for all cases in which one can think to deal with 10^{10} *or* $10^{10^{10}}$ *elements in a cubic millimeter or even with billions of times more; hence they are particularly invaluable in the frame of Geometry, which must equally well adapt to deal with the most diverse physical cases in which the number of the elements can be widely different. Often in the use of all such models, created in this way, it is necessary to put aside the basic concept, from which they have overgrown, and perhaps to forget it entirely, at least temporarily. But I think that it would be a mistake to think that one could become free of it entirely.*"

The latter sentence also reminds us that the evaluation of the corrections is of course a harder problem, which it would be a mistake to set aside. In fact the corrections are quite important and somehow even more important than the continuum models theselves, which will remain as a poor idealization of far more interesting cooperative phenomena (see, for instance, the microscopic theory of phase separation in the Ising model, [Gallavotti, 2000]).

The discrete conceptions of Boltzmann, perfectly meaningful mathematically, were apparently completely misunderstood by his critics: yet it was clearly stated for instance in the analysis of the Loschmidt remarks on irreversibility [Boltzmann, 1877a, #39], or in one of the replies to Zermelo, [Boltzmann, 1896, #119,1896], and in the book on gases, [Boltzmann, 1964, 1896], see also [Gallavotti, 1995].

But the seed had been sown and the discrete phase space and the ergodic hypothesis became unseparable.

10 Thermodynamic analogies. Ensembles,

The notion of thermodynamic analogy, or model of thermodynamics, was formulated and introduced by Helmoltz for general systems admitting only periodic motions (called *monocyclic*), [Helmholtz, 1895a,b].[27]

Thermodynamic analogy: *Given a Hamiltonian system and a collection* $\mathcal{E}$ *of invariant probability distributions on phase space depending on parameters* $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \ldots)$ *denoted* $\mu_{\boldsymbol{\alpha}}$ *let* $U(\boldsymbol{\alpha}), V(\boldsymbol{\alpha}), p(\boldsymbol{\alpha}), T(\boldsymbol{\alpha})$ *be* $\mu_{\boldsymbol{\alpha}}$*-average values*

[27] However the notion had been developed earlier although not formalized, by Boltzmann already in 1866, and by Clausius in 1871. It is clearly used, again without a formal definitition, in [Boltzmann, 1871d, #20] and again developed in [Boltzmann, 1877a, #39], where also an explicit example is discussed.
It is possible that Boltzmann did not claim priority over Helmoltz' work not only because he had become older, hence wiser, but also because he wrote this paper while he was in contact with Helmoltz who was inviting him to accept a professorship in Berlin: I conjecture that he had started the 1884 work to establish a closer scientific contact with Helmoltz but, while thinking to it, he realized that he could go far beyond the monocyclic systems and formalized and unified into a fully developed theory of ensembles his older theory of the microcanonical ensemble, built on the combinatorial count of the microscopic configurations in [Boltzmann, 1868a, #5] and [Boltzmann, 1877b, #42], and of the canonical and microcanonical ensembles built on a form of the ergodic hypothesis in [Boltzmann, 1871d, #20]. and the other "trilogy" papers.

of suitable observables. If $\boldsymbol{\alpha}$ *is varied by* $d\boldsymbol{\alpha}$ *let* dU, dV, dp, dT *be the corresponding variations of* $U(\boldsymbol{\alpha}), V(\boldsymbol{\alpha}), p(\boldsymbol{\alpha}), T(\boldsymbol{\alpha})$. *Then the "ensemble" of the distributions* $\mu_{\boldsymbol{\alpha}}$ *and the functions* $U(\boldsymbol{\alpha}), V(\boldsymbol{\alpha}), p(\boldsymbol{\alpha}), T(\boldsymbol{\alpha})$ *describe a thermodynamic analogy if*

$$\frac{dU + pdV}{T} \;=\; \textit{exact differential} \qquad (@)$$

i.e. if there is a function $S(\boldsymbol{\alpha})$ *such that* $dS = \frac{dU+pdV}{T}$.

An example, actually illustrating the early works of Boltzmann and Clausius, is in Sec.5 above.

The wide generality of the notion provided a new perspective, and grounds, to make popular the theory of the ensembles, and to show that the thermodynamic relations would hold in *most mechanical systems*, from the small and simple to the large and complex.

In the first cases the relations would be trivial identities of no or little interest, just *thermodynamic analogies*, but in the large systems they would become nontrivial and interesting being relations of general validity. In other words they would be a kind of symmetry property of Hamiltonian Mechanics.

Then in the fundamental paper [Boltzmann, 1884, #73], following and inspired by the quoted works of Helmoltz, Boltzmann was able to achieve what I would call the completion of his program of deducing the second law, Eq.(@), from Mechanics. In simple monomolecular systems:

(1) the *absolute temperature* T is identified with the average kinetic energy over the periodic motion following the initial datum $(\mathbf{p}, \mathbf{q})$ of a macroscopic collection of N identical particles interacting with a quite *arbitrary* pair interaction, and
(2) the *energy* U is $H(\mathbf{p}, \mathbf{q})$ sum of kinetic and of a potential energy,
(3) the *volume* V is the volume of the region where the positions $\mathbf{q}$ are confined (typically by a V-dependent hard wall potential),
(4) the potential energy of interaction is φ_V, usually dependent on the volume V, and the *pressure* p is the average of $-\partial_V \varphi_V$ (with the interpretation of force exercized on the walls by the colliding particles),

then, from the assumption that each phase space point would evolve periodically visiting every other point on the energy surface (*i.e.* assuming that the system could be regarded as ergodic in the sense of Sec.8 or monocyclic in Helmoltz' sense) it would follow that the quantity p could be identified with the $\langle\, -\partial_V \varphi_V \,\rangle$, time average of $-\partial_V \varphi_V$, and Eq.(@) would follow as a *heat theorem*.

The heat theorem would therefore be a consequence of the general properties of monocyclic systems, which already in the 1866 work of Boltzmann had been shown to generate a thermodynamic analogy.

This led Boltzmann to realize, in the same paper, that there were a large number of mechanical models of thermodynamics: the macroscopic states could be identified with regions whose points would contribute to the average values of quantities with thermodynamic interpretation (*i.e.* p, V, U, T) with a weight (hence a probability) also invariant under time evolution.

Hence imagining the weights as a density function one would see the evolution as a motion of phase space points, each representing possible atomic configuration, leaving the density fixed. Such distributions on phase space were called *monodic*, because they keep their identity with time or, as we say, are invariant.

And in [Boltzmann, 1884, #73] several *collections* $\mathcal{E}$ of weights or *monodes* were introduced: today we call them invariant distributions on phase space or *ensembles*. Among the ensembles $\mathcal{E}$, *i.e.* collections of monodes, Boltzmann singled out the ensembles called *orthodes* ("behaving correctly"): they were the families $\mathcal{E}$ of probability distributions on phase space depending on a few parameters (normally 2 for simple one component systems) such that the corresponding averages p, V, U, T, defined in (1-4) above, would vary when the parameters were varied. And the variations dU, dV of average energy and volume would be such that the *r.h.s* of Eq.(@) would be an exact differential, thereby defining the *entropy* S as a function of state, see [Gallavotti, 1995, 2000].

The ergodic hypothesis yields the "orthodicity" of the ensemble $\mathcal{E}$, that today we call *microcanonical* (in [Boltzmann, 1884, #73] it was named *ergode*): but ergodicity, *i.e.* the dynamical property that evolution would make every phase space point visit every other, was not necessary to the orthodicity proof of the ergode: *but it is necessary for its physical interpretation* of a distribution that describes an equilibrium state with given macroscopic parameters.

In fact in [Boltzmann, 1884, #73] the relation Eq.(@) is proved directly without recourse to dynamical properties (just as we do today, see [Fisher, 1964, Ruelle, 1968, Gallavotti, 2000] and AppendixJ below); and in the same way the orthodicity of the *canonical ensemble* (called *holode* in [Boltzmann, 1884, #73]) was obtained and shown to generate a Thermodynamic analogy which is equivalent (for large enough systems) to the one associated with the microcanonical ensemble.[28]

In the end in [Boltzmann, 1868a, 1871c, 1877a, 1868-71] and, in final form, in [Boltzmann, 1884, #73] the theory of ensembles and of their equivalence was born without need of the ergodic property: however its still important role was to guarantee that the quantities p, V, U, T, S defined by orthodic averages with respect to invariant distributions on phase space had the physical meaning implied by their names. This was true for the microcanonical ensemble (or

[28] Still today a different interpretation of the word "ensemble" is widely used: the above is based on what Boltzmann calls "*Gattung von Monoden*", see p.132,l.14 of [Boltzmann, 1884, #73]: unfortunately he is not really consistent in the use of the name "monode" because, for instance in p.134 of the same reference, he clearly calls "monode" a collection of invariant distributions rather than a single one; further confusion is generated by a typo on p.132,l.22, where the word "ergode" is used instead of "holode" while the "ergode" is defined only on p.134. It seems beyond doubt that "holode" and "ergode" were intended by Boltzmann to be *collections* $\mathcal{E}$ of invariant distributions (parameterized respectively by U, V or by $(k_B T)^{-1}, V$, in modern notations): Gibbs instead called "ensemble" each single invariant distribution (*i.e.* a "monode", as a family of identical non interacting systems filling phase space with an invariant density), or at least that is what is often stated. Although the original names proposed by Boltzmann may be more appropriate, of course, we must accept calling "microcanonical ensembles" the elements of ergode and "canonical ensembles" those of the holode, see [Gallavotti, 2000], but I would prefer replacing the word ensemble by distribution.

"ergode") by the ergodic hypothesis, and followed for the other ensembles by the equivalence.

Unfortunately the paper [Boltzmann, 1884, #73] has been overlooked until quite recently by many, actually by most, physicists.[29] See p.242 and p.368 in [Brush, 1976] for an exception, perhaps the first.

Of course conceiving phase space as discrete is essential to formulate the ergodicity property in a mathematically and physically acceptable way: it does not, however, make it easier to prove it, even in the discrete sense just mentioned (nor in the sense acquired later when it was formulated mathematically for systems with continuous phase space).

It is in fact very difficult to be *a priori* sure that the dynamics is an evolution which has only one cycle. Actually this is very doubtful: as one realizes if one attempts a numerical simulation of an equation of motion which generates motions which are ergodic in the mathematical sense, like motions in convex billiards, [Sinai, 1977].

And the difficulty is already manifest in the simpler problem of simulating differential equations in a way which rigorously respects the uniqueness theorem. In computers the microscopic states are rigorously realized as regular cells (because points are described by integers, so that the cells sizes are limited by the hardware performance and software precision) and phase space is finite. By construction, simulation programs map a cell into another: but it is extremely difficult, and possible only in very special cases (among which the only nontrivial that I know is [Levesque and Verlet, 1993]) without dedicating an inordinate computing time to insure a $1-1$ correspondence between the cells.

Nevertheless the idea that phase space is discrete and motion is a permutation of its points is very appealing because it gives a privileged role to the *uniform distribution* on the phase space region in which the motion develops, *i.e.* the energy surface, if the ergodic hypothesis holds, assuming it discretized on a regular lattice.

Furthermore the hypothesis has to be supplemented with the realization, made possible by the discretization of phase space which allows a detailed combinatorial analysis, that its predictions can be checked on short time scales because they are properties of most microscopic configurations, making the unobservable recurrence time irrelevant.

The success of the ergodic hypothesis has several aspects. One that will not be considered further is that it is not necessary: this is quite clear as in the end we want to find the relations between a very limited number of observables and we do not need for that an assumption which tells us the values of all possible averages, most of which concern "wild" observables (like the position of a tagged particle). The consequence is that the ergodic hypothesis is intended in the sense that confined Hamiltonian systems "can be regarded as ergodic for the purpose of studying their equilibrium properties".

[29] Possibly because it starts, in discussing the thermodynamic analogy, by giving the Saturn rings as an "example": a brilliant one, certainly but perhaps discouraging for the suspicious readers of this deep and original paper on Thermodynamics.

Remark: The above historical analysis is concentrated on the ergodic hypothesis and only touches the theory of the ensembles in the years following 1884: hence the role of Gibbs, Planck, Einstein ..., as well as the natural role played in quantum mechanics by Boltzmann's initial view on microscopic motion periodicity, [L. de Broglie, 1995], is not even mentioned here. A very detailed study mostly centered on the development of the theory of the ensembles has recently appeared, [Inaba, 2015].

11 From equilibrium to stationary monequilibrium

What is, perhaps, the most interesting aspect of the Ergodic Hypothesis formulated imagining space-time and phase space as a *regular array of points* is that it can hold for systems of any size and lead to relations which are essentially size independent as well as model independent and which become interesting properties when considered for macroscopic systems.

Is it possible to follow the same path in studying nonequilibrium phenomena?

The simplest such phenomena arise in stationary states of systems subject to the action of nonconservative forces and of suitable heat-removing forces (*i.e.* "thermostats", whose function is to forbid indefinite build up of energy in the system).

Such states are realized in Physics with great accuracy for very long times, in most cases longer than the available observation times. For instance it is possible to keep a current circulating in a wire subject to an electromotive force for a very long time, provided a suitable cooling device is attached to the wire.

As in equilibrium, the stationary states of a system will be described by a collection $\mathcal{E}$ of probability distributions μ on phase space, invariant with respect to the dynamics, which I continue to call *ensemble*: the distributions $\mu \in \mathcal{E}$ will be parameterized by a few parameters $U, V, E_1, E_2, \ldots$ which have a physical interpretation of (say) average energy, volume, intensity of the nonconservative forces acting on the system (that will be called "external parameters").

Each distribution μ will describe a macroscopic state in which the averages of the observables will be their integrals with respect to μ. The equations of motion will be symbolically written as

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$$

and we shall assume that $\mathbf{f}$ is smooth, that it depends on the external parameters and that the phase space visited by trajectories is bounded (at fixed external parameters and initial data).

Since we imagine that the system is subject to nonconservative forces the phase space volume (or any measure with density with respect to the volume)

will not be preserved by the evolution and the divergence

$$\sigma(\mathbf{x}) = -\sum_i \partial_{x_i} f_i(\mathbf{x})$$

will be *different* from 0. We expect that, in interesting cases, the time average σ_+ of σ will be positive:[Ruelle, 1996, 1997]

$$\sigma_+ \stackrel{def}{=} \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \sigma(S_t\mathbf{x})\, dt \;>\; 0\,.$$

and, with "few" exceptions, $\mathbf{x}$–independent.

This means that there cannot be invariant distributions that can be represented by a density with respect to the volume. And the problem to find even a single invariant distribution is nontrivial except possibly for some concentrated on periodic orbits.

Occasionally an argument is found whereby, in equilibrium, motion can be regarded as a permutation of cells "because of the volume conservation due to Liouville's theorem". But this cannot be a sensible argument due to the chaoticity of motion: it cannot be ignored (whether in equilibrium or in nonequilibrium states) that any volume element will be deformed under evolution and stretched along certain directions while it will be compressed along others. Therefore the points of the discretized phase space should not be thought as small volume elements, "cells" with positive volume, but precisely as individual (0 volume) points which the evolution permutes.

The problem can be attacked, possibly, by following again Boltzmann's view of dynamics as discrete, ("*die Zahl der lebendigen Kräft ist eine diskrete*", see p.167 in [Boltzmann, 1877b, #42]).

12 Nonequilibrium and discrete phase space

In a discrete conception, points in phase space *are not extended cells* but they evolve as points without dimension. *This has become a common way of imagining dynamical systems, particularly because of the development of simulations.*

Simulations have played a key role in the recent studies on nonequilibrium. And simulations operate on computers to perform solutions of equations in phase space: therefore phase space points are given a digital representation which might be very precise but rarely goes beyond 32 bits per coordinate. If the system contains a total of N particles each of which needs 4 coordinates to be identified (in the simplest 2–dimensional models, 6 otherwise) this gives a phase space (virtually) containing $\mathcal{N}_{tot} = (2^{32})^{4N}$ points which cover a phase space region of desired size V in velocity and L in position with a lattice of mesh $2^{-32}V$ or $2^{-32}L$ respectively.

Therefore the "*fiction*" of a discrete phase space, used first by Boltzmann in his foundational works, [Boltzmann, 1877b, #42,p.167], has been taken extremely seriously in modern times with the peculiarity that it is seldom even mentioned in the numerical simulations.

A simulation for a system of $\mathcal{N}_{tot}$ atoms is a code that operates on discrete phase space points transforming them into other points. In other words it is a map $\overline{S}$ which associates with any point on phase space a new one with a precise deterministic rule that can be called a *program* or *code*.

All programs for simulating solutions of ordinary differential equations have some serious drawbacks: for instance, as mentioned above, it is very likely that the map $\overline{S}$ defined by a program is not invertible, unlike the true solution to a differential equation of motion, which obeys a uniqueness theorem: different initial data might be mapped by $\overline{S}$ into the same point.

Since the number $\mathcal{N}_{tot}$ is finite, all points will undergo a motion, as prescribed by the program $\overline{S}$, which will become *recurrent*, *i.e.* will become eventually a permutation of a subset of the phase space points, hence *periodic*.

The ergodic hypothesis was born out of the natural idea that the permutation would be a *one cycle* permutation: every microscopic state would recur and continue in a cycle, [Gallavotti, 1995]. In simulations, even if dealing with discretized time reversible systems, it would not be reasonable to assume that all the phase space points are part of a permutation, because of the mentioned non invertibility of essentially any program. It is nevertheless possible that, once the *transient* states (*i.e.* the ones that never recur, being out of the permutation cycles) are discarded and motion reduces to a permutation, then the permutation is just a single cycle one.

So in simulations of motions of isolated systems an ergodic hypothesis can be defined and it really consists in two parts: first, the non recurrent phase space points should be "negligible" and, second, the evolution of the recurrent points consists in a single cycle permutation. Two comments:
(a) Periodicity is not in contrast with chaotic behavior: this is a point that Boltzmann and others (*e.g.* Thomson (Lord Kelvin)) clarified in several papers ([Boltzmann, 1877a, #39],[Thomson, 1874], for the benefit of the few that at the time listened.
(b) The recurrence times are beyond any observable span of time (as soon as the particles number N is larger than a few units), [Boltzmann, 1964, Sec.88].

In presence of dissipation, motions in models based on a continuum space-time, develop approaching a subset of phase space, *the attracting set* A,[30] and on it the attractor B, which has therefore zero volume: because volume is not invariant and is asymptotically, hence forever, decreasing.

In general the *nonrecurrent points will be "most" points*: because in presence of dissipation the attractor set will have 0 volume, (even in the cases in which the attracting set $\mathcal{A}$ is the entire phase space, like in the small perturbations of conservative Anosov systems, [Arnold and Avez, 1968, Sinai, 1977]).

[30] The notion of attracting set $\mathcal{A}$ and of attractor for a system whose evolution is governed by an ordinary differemtial equation are sometimes identified: it is however useful to recall the definitions. An attracting set $\mathcal{A}$ is a closed set such that all initial data close enough to it (*i.e.* in a domain of attraction U) evolve in time so that their distance to $\mathcal{A}$ tends to 0. If points chosen randomly in a domain of attraction of $\mathcal{A}$, with a probabilty with a density with respect to the volume, evolve in time generating on $\mathcal{A}$ a *unique* statistical distribution μ, then any invariant subset B of $\mathcal{A}$ which has μ-probability 1 ($\mu(B) = 1$) is called an attractor. Of course in a discrete model of evolution the two notions coincide.

Nevertheless in the discrete form the ergodic hypothesis can be extended and formulated also for general nonconservative motions, see below.

13 Nonequilibrium: the ergodic hypothesis

The above considerations suggest the following extension of the ergodic hypothesis: it can be formulated by requiring that

Ergodic hypothesis (equilibrium and nonequilibrium): *In a phase space discretized on a regular lattice*[31] *non recurrent points are negligible and the recurrent points form the attracting set and are cyclically permuted forming a one cycle permutation.*

Since empirically most systems. in equilibrium as well as out of equilibrium, show chaotic motions it is convenient to assume that, aside from exceptions, systems satisfy the stronger:

Chaotic hypothesis: *The above ergodic hypothesis holds and furthermore the motion on the attracting set is supposed chaotic.*

Mathematically "chaotic" means that the attracting set can be imagined as a surface and that the motion on it is hyperbolic, see [Gallavotti, 2014] (for history and developments).[32]

In the latter situations the statistics of the motions will be *uniquely determined* by assigning a probability $\mathcal{N}^{-1}$ to each of the $\mathcal{N}$ configurations on the (discrete version of the) attractor: and this will be the *unique* stationary distribution, providing also an answer to the question raised already by Boltzmann, [Boltzmann, 1871b, #8,p.255], in the early days.

Remarks: (1) The uniqueness of the stationary distribution is by no means obvious and, as well, it is not obvious that the motion can be described by a permutation of the points of a regularly discretized phase space. Not even in equilibrium.
(2) Boltzmann argued, in modern terms, that after all we are interested in very few observables, in their averages and in their fluctuations. Therefore we do not have to follow the details of the microscopic motions and all we have to consider are the time averages of a few physically important observables $F_1, F_2, \dots, F_q$, with q small. This means that we have to understand what is now called a *coarse grained* representation of the motion, collecting together all points on which the observables $F_1, F_2, \dots, F_q$ assume the same values. Such collection of microscopic states is called a *macrostate*, [Lebowitz, 1993, Garrido et al., 2005].

[31] As commented above the discretization on a regular lattice is essential and simply reflects our empirical evidence that the systems must be equivalently described by the usual ordinary differential equations.

[32] Hyperbolic means that every point is the intersection of the phase space velocity with two surfaces, W_u, W_s, transversal to it and which expand/contract, as time t elapses, under the evolution map S_t at a minimum rate $\lambda > 0$.

The reason why motion appears to reach stationarity and to stay in that situation is that for the overwhelming majority, [Boltzmann, 1877a, Uhlenbeck, 1968], of the microscopic states, *i.e.* points of a discretized phase space, the interesting observables have the same values. The deviations from the averages are observable over time scales that are most often of humanely appreciable size and have nothing to do with the recurrence times. Boltzmann gave a very clear and inspiring view of this mechanism by developing "Boltzmann's equation", [Boltzmann, 1872, #22]: perhaps realizing its full implications only a few years later when he had to face and overcome the conceptual objections of Loschmidt and others, [Boltzmann, 1877a, #39].

A development of the above chaotic hypothesis together with some of its consequences, including few implications on the theory of fluctuations, can be found in the review [Gallavotti, 2014]. The first among the consequences is the identification of the statistics of the stationary states of the systems: which can considered valid for nonequilibrium as well as for equilibrium (where it coincides with the microcanonical Gibbs state). And it can be viewed as the discretized version of Ruelle's theory of chaotic dynamical systems, [Ruelle, 1989, 1995, 2003] and originated in [Ruelle and Takens, 1971].

The discrete conception of phase space also allows, assuming the chaotic hypothesis, to count the number $\mathcal{N}$ of configurations in the attracting sets and to ask the question whether entropy can be defined proportionally to $\log\mathcal{N}$ as in equilibrium: in [Gallavotti, 2014] a (controversial) negative conclusion is reached together with the (positive) argument that, neverthess, the evolution towards stationarity might have a Lyapunov function (actually many) related to $\log\mathcal{N}$, see [Gallavotti, 2014].

The alternative view that entropy should make sense as a function of the state, possibly defined up to a constant, *whether in equilibrium or in a stationary non equilibrium* or even for non stationary states is held by many physicists since a long time, see for instance the view of Planck, [Dugas, 1959, p.239].

Appendices

A Boltzmann' priority claim (vs. Clausius)

Translation and comments on: *Zur priorität der auffindung der beziehung zwischen dem zweiten hauptsatze der mechanischen wärmetheorie und dem prinzip der keinsten wirkung*, 1871, [Boltzmann, 1871a, #17,p.228-236].

Incipit:

Mr. Clausius presented, at the meeting of 7 Nov. 1870 of the "Niederrheinischen Gesellschaft für Natur und Heilkunde vorgetragenen" and in Pogg. Ann. **142**, S. 433, [Clausius, 1872], a work where it is proved that the second fundamental theorem of the mechanical theory of heat follows from the principle of least action and that the corresponding arguments are identical to the ones implying the principle of least action. I have already treated the same question in a publication of the Wien Academy of Sciences of 8 Feb. 1866, printed in the volume 53 with the title *On the mechanical meaning of the second fundamental theorem of the theory of heat*, [[Boltzmann, 1866, #2]];[33] and I believe I can assert that the fourth Section of my paper published four years earlier is, in large part, identical to the quoted publication of Mr. Clausius. Apparently, therefore, my work is entirely ignored, as well as the relevant part of a previous work by Loschmidt. It is possible to translate the notations of Mr. Clausius into mine, and via some very simple transformation make the formulae identical. I claim, to make a short statement, that given the identity of the subject nothing else is possible but some agreement. To prove the claim I shall follow here, conveniently, the fourth section of my work of 8 Feb. 1866, of which only the four formulae Eq.(23a),(24a),(25a) and (25b), must be kept in mind.[34]

To compare this work with Mr. Clausius' we must first translate into each other the notations. The signs d and δ are used by Mr. Clausius in my same sense; except that for me the signs δ indicate a general variation while Mr. Clausius considers variations of a very special kind, by suitably arranging the times of the varied state which will be compared with those of the initial state. Once such special kind of variations is employed it results that, for Mr. Clausius, the variation of the average of a quantity equals the average of the variation. Likewise we indicate all the quantities that refer to Thermodynamics $(Q, T, L, Z, S, ...)$ in the same sense. The time that an atom spends, on its closed trajectory, I denote $t_2 - t_1$, and Mr. Clausius denotes it by i, the average kinetic energy of

[33] *A clear exposition of this work can be found in Dugas' book, [Dugas, 1959, p.153-157]; see also [Gallavotti, 2014] where the translation error on p.132, l.21 "...site of the region occupied by the body..." should be replaced by "..., whatever the state of the body...".*

[34] *The answer in [Clausius, 1872], commented in appendixB below, was to apologize for having been unaware of Boltzmann's work and pointed out that Boltzmann's formulae became equal to his own after a suitable interpretation, requiring assumptions not needed in his work; furthermore his version was more general than his: certainly, for instance, his analysis takes into account possible variations of external forces.*

an atom I indicate by

$$\frac{1}{t_2-t_1}\int_{t_1}^{t_2}\frac{mc^2}{2}dt, \quad \text{Mr. Clausius by} \quad \frac{m}{2}\overline{v^2}$$

To make notations of my formulae conform to those of Mr. Clausius it can be set

$$(A)\quad \begin{cases} i & \longleftrightarrow & t_2-t_1, \\ i\dfrac{m}{2}\overline{v^2} \text{ or } ih & \longleftrightarrow & \displaystyle\int_{t_1}^{t_2}\frac{mc^2}{2}dt, \\ i\overline{X\delta x+Y\delta y+Z\delta z} & \longleftrightarrow & \displaystyle\int_{t_1}^{t_2}(X\delta x+Y\delta y+Z\delta z) \end{cases}$$

The first notable formulae, to which Mr. Clausius arrives, are his formulae (17),(18) and (19), which are identical to the first of the equalities (22) of my work: they are mapped into each other by the sustitutions (A); in fact my formula (22) so becomes:

$$i\frac{m}{4}\overline{\delta v^2}=\frac{i\varepsilon}{2}+\frac{i}{2}\overline{X\delta x+Y\delta y+Z\delta z}.$$

Multiply by $\frac{2}{i}$ and consider that, by the method of variation of Mr. Clausius, $\overline{\delta v^2}=\delta\overline{v^2}$, so that

$$\frac{m}{2}\delta\overline{v^2}=\varepsilon+\overline{X\delta x+Y\delta y+Z\delta z} \tag{1}$$

The quantity ε coincides with the one in my formula (23a) which by the translation table (A) becomes

$$\varepsilon=\frac{2\delta(i\frac{m}{2}\overline{v^2})}{i}=\frac{\delta i}{i}m\overline{v^2}+m\delta\overline{v^2}.$$

Substitute these values in equation (1) above and shift all on the left of the equalities, so it immediately follows:

$$\overline{X\delta x+Y\delta y+Z\delta z}+\frac{m}{2}\delta\overline{v^2}+\frac{\delta i}{i}m\overline{v^2}=0$$

which is identical to the equations (17),(18) and (19) of the work of Mr. Clausius. By the successive introduction of the quantities that are customary in the mechanical theory of heat, we isolate first what I call the heat produced δQ and subsequently the work performed is subtracted, while Mr. Clausius follows the inverse order. However the total heat amount transferred equals the sum of the increase of kinetic energy and of the amount of work received, so that it is not difficult to follow the context. Namely I define the quantity ε as the amount of heat received by the body (*i.e.* my two statements "let now an atom receive an infinitely small amount of kinetic energy ε and in this way the work done and the increase of kinetic energy are accounted" and "therefore the sum of all the ε

equals the whole quantities of heat received, measured in units of work"). The quantity ε is then, by my equation (22):

$$\varepsilon = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} dt\delta \frac{mv^2}{2} - \int_{t_1}^{t_2} \frac{1}{t_2 - t_1} dt(X\delta x + Y\delta y + z\delta z)$$

Thus I intend that the amount of heat received by the atom is the sum of the average increment of its kinetic energy and the average of $-(X\delta x + Y\delta y + z\delta z)$. Hence it immediately follows that the work output corresponding to the amount of heat δL, average of $-(X\delta x + Y\delta y + z\delta z)$, is therefore in Mr. Clausius notations $\delta\overline{U}$, and this is so also in Mr. Clausius [see his equation (20)]; and again I say: "if the balance was not even, we could wait long enough, until thermal equilibrium or stationary flow are reached, and then extract the average increase in excess on what was denoted ε, per atom". I also state, as ahead Mr. Clausius, that the amount of heat is not realized in just one phase [phase in the sense of Clausius] and define ε as the total heat intaken. Also in the theoretical interpretation of the mechanical propositions we do not differ, although Mr. Clausius puts his equation in a somewhat different and more detailed way. I can also bring these to comparison. I consider the quantity δL only for many material points, and I develop it in formula (25a). To obtain the formula for one atom, we take out the summation signs. Then we take again the change of notations (A), so my formula (25a) is changed in

$$\delta L = \frac{\delta(ih)}{i} + h\frac{\delta i}{i}$$

or in the construction of the variation:

$$\delta L = \delta h + 2h\delta \log i$$

wherein immediately are recognized the equations (21),(22) and (23) of Mr. Clausius. Hence we obtain the disgregation of a material point, as we bring in my formula (25) the substitution (A) and drop the summation signs. The mentioned formula becomes then

$$Z = \log(hi) + \log i = \log(hi^2)$$

which again immediately matches with that of Mr. Clausius for the development of the equation (24) (24) for the value found for the Disgregation.

I will now remark, that the fact that the forces X, Y, Z in my calculation likewise are seen subject to variations (which, according to Mr. Clausius' expression, vary the ergal), indeed about this I said:

"At the same time suppose an infinitely small variation of the volume and pressure of the body", of which it was already discussed, as indeed the forces acting on the body in general should change, because generally, as long as these forces stay unchanged, there is only a single independent variable, so

that we cannot speak of complete or incomplete differential.[35] Hence it is to mention that I dedicate, again as Mr. Clausius, my proposition to treat a single material point which, while it invariantly describes a closed path, will undergo an infinitely small increase of kinetic energy and at the same time the action of the acting forces changes. Since a change of the atomic interactions in nature does not happen I confine myself in performing the calculations to never give up their constancy, and to add that the pressure can change.[36] Here Mr.Clausius obtains the advantage that there is the possibility of having stressed explicitly such change.

Now Mr. Clausius comes to speak of the principle of least action. He says setting up some remarks:
"This equation has the form that for a single moving point the theorem of least action prescribes. However in the meaning there is a difference, as by the solution of our equations we have assumed that the initial and varied motions develop in closed paths, that in no point are fixed [in particular do not have extermes fixed] while by the least action proposition it is supposed that both paths have a common starting point and a common endpoint. But this distinction is irrelevant, and the solution of the equation (24) under both assumptions can be carried in equal way, if the period i which the moving point needs to come from the initial location to the end location stays the same for the initial motion and for the varied one".

This analogy with the principle of least action naturally could not escape me. My words are the following:

"It is easily seen that our conclusion on the meaning of the quantities that intervene here is totally independent from the theory of heat, and therefore the second fundamental theorem is related to a theorem of pure mechanics to which it corresponds just as the kinetic energy principle [energy conservation] corresponds to the first principle; and, as it immediately follows from our considerations, it is related to the least action principle, in a form somewhat generalized about as follows. If a system of point masses under the influence of forces, for which the kinetic energy principle holds, performs some motion, and if then all points undergo an infinitesimal variation of the kinetic energy and are constrained to move on a path infinitely close to the precedent, then

$$\delta \sum \frac{m}{2} \int c\, ds$$

equals the variation of the total kinetic energy multiplied by half the time in-

[35] *Here Boltzmann says that, if no external force is allowed to vary, the amount $\frac{dQ}{T}$ depends on only one parameter, say on the temperature, and is necessarily an exact differential. Yet Clausius complaint that Boltzmann mentions variation of external forces "en passant" and then forgets about it is appropriate. The justification that it was enough to mention that external forces variations could be present is not accepted by Clausius, nevertheless it seems quite convincing after some thought: but Boltzmann had been too fast. Actually external forces are mentioned again in the 1866 paper towards the end of the paper in discussing the action principle, see below.*

[36] *In other words Boltzmann admits that he has not considered varying external forces, but claims to have done so for simplicity.*

terval during which the motion develops, when the sum of the product of the displacements of the points times their speeds and the cosine of the angles on each of the path elements are equal, for instance the points of the new path elements are on the normal of the old paths. This proposition gives, for the kinetic energy transferred and if the variation of the limits of integration vanishes, the least action principle in the usual form."[37]

It is seen that the type and kind that I call proposition, has nature identical with that of Mr. Clausius, but my proposition is somewhat more general. It is in fact clear that if, as Mr. Clausius assumes, the old and new paths are closed every one of my conditions holds.

Now, in the work of Mr. Clausius, the change from a single material point to a system of points, follows. Also here the following difference from my work does not touch the nature of the matter. So I set the average kinetic energy of an atom as directly equal to its temperature, Mr. Clausius instead sets it equal to the temperature multiplied by a constant factor mc, where the factor m has the purpose of fixing a temperature unit and the factor c to conform to the observations (namely those of Kopps) of the exceptions to the Dulong-Petit's law. Let us leave aside the question about the cause of the exceptions: it is anyway clear that the introduction of such factors would modify our analysis of the second main proposition in an entirely irrelevant way. Only the transition from closed paths to not closed paths is treated by Mr. Clausius in a way different from mine, indeed the applicability for not closed paths of the equalities

$$\int_{t_1}^{t_2} \frac{mc^2}{2} \cdot dt = \int_{\tau_1}^{\tau_2} \frac{mc^2}{2} \cdot dt$$

to the heat problem still deserves an exact proof. Similar to the derivation of Mr. Clausius, there is a passage in a work presented on 25 February 1869 at the Wiener Akademie der Wissenshaften by Loschmidt, where he discusses a second representation of my entire final method (Sitzungberichte der Wiener Akad., Bd. 59).

Here I will add a list of my final formulae compared to those of Mr. Clausius. Mr. Clausius denotes the average kinetic energy of an atom with mcT, while I denote it by

$$\frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \frac{mc^2}{2} dt$$

Also, to make the notations match, if must be written in my formulae

$$(B) \qquad \begin{cases} i & \Rightarrow & t_2 - t_1 \\ mcTi & \Rightarrow & \displaystyle\int_{t_1}^{t_2} \frac{mc^2}{2} dt\rho \end{cases}$$

[37] *Nevertheless it seems improper to say that we are dealing with an extension of the least action principle: the latter determines the equations of motion while here a relation is established between two motions which are close and which satisfy the equations of motion.*

therefore the first of the formulae (24) becomes:

$$\delta Q = 2 \sum \frac{\delta(mcTi)}{i}$$

or by multiplication by T and division of the same quantity under the signs of summation (as I use that T has the same value for all points)

$$\delta Q = 2T\delta \sum mc \log Ti,$$

which is identical with formula (35) of Mr. Clausius. My formula (24a) gives us the entropy. Denoting it by S and using the notations of Mr. Clausius, we obtain therefore

$$S = 2 \sum mc \log(Ti) + C$$

which formula coincides with the equality (36) of Mr. Clausius. The caloric equivalent of work is missing, as I measure heat in mechanical units. Using the change of notations (B) in my formula (25a), we obtain

$$\delta L = \sum \frac{\delta(mcTi)}{i} + \sum mcT\frac{\delta i}{i} = T\delta \sum mc \log(Ti^2),$$

as the formula (34) of Mr. Clausius, whose division by T gives us likewise the disgregation [free energy] in agreement with Mr. Clausius. I think to have here proven my priority on the discovery of the mechanical meaning of the second law and I can finally express my pleasure over that, if an authority of the level of Mr. Clausius contributes to the diffusion of the knowledge of my works on the mechanical theory of heat.

Graz, 16 May 1871.

B Clausius' reply (to Boltzmann's claim)

Translation and comments on: R. Clausius *Bemerkungen zu der prioritätreclamation des Hrn. Boltzmann*, Pogg. Ann. **144**, 265–274, 1871.

In the sixth issue of this Ann., p.211, Mr. Boltzmann claims to have already in his 1866 paper reduced the second main theorem of the mechanical theory of heat to the general principles of mechanics, as I have discussed in a short publication. This shows very correctly that I completely missed to remark his paper, therefore I can now make clear that in 1866 I changed twice home and way of life, therefore naturally my attention and my action, totally involuntarily, have been slowed and made impossible for me to follow regularly the literature. I regret overlooking this all the more because I have subsequently missed the central point of the relevant paper.

It is plain that, in all point in which his work overlaps mine, the priority is implicit and it remains only to check the points that agree.

In this respect I immediately admit that his expressions of disgregation [*free energy*] and of entropy overlap with mine on two points, about which we shall definitely account in the following; but his mechanical equations, on which such expressions are derived are not identical to mine, of which they rather are a special case.

We can preliminarily limit the discussion to the simplest form of the equations, which govern the motion of a single point moving periodically on a closed path.

Let m be the mass of the point and let i its period, also let its coordinates at time t be x, y, z, and the acting force components be X, Y, Z and v its velocity. The latter quantities as well as other quantities derived from them, vary with the motion, and we want to denote their average value by over-lining them. Furthermore we think that near the initially considered motion there is another one periodic and infinitesimally different, which follows a different path under a different force. Then the difference between a quantity relative to the first motion and the one relative to the varied motion will be called "variation of the quantity", and it will be denoted via the symbol δ. And my equation is written as:

$$-\overline{X\,\delta x + Y\delta\, y + Z\,\delta Z} = \frac{m}{2}\delta\overline{v^2} + m\overline{v^2}\delta\log i \qquad (I)$$

or, if the force acting on the point admits an ergale [*potential*], that we denote U, for the initial motion,[38]

$$\delta\overline{U} = \frac{m}{2}\,\delta\overline{v^2} + m\,\overline{v^2}\,\delta\log i \qquad (Ia)$$

Boltzmann now asserts that these equations are identical to the equation that in his work is Eq.(22), if elaborated with the help of the equation denoted (23a). Still thinking to a point mass moving on a closed path and supposing it modified into another for which the point has a kinetic energy infinitely little different by the quantity ε, then Boltzmann's equation, after its translation into my notations, is

$$\frac{m}{2}\overline{\delta v^2} = \varepsilon + \overline{X\,\delta x + Y\delta\, y + Z\,\delta Z} \qquad (1)$$

and thanks to the mentioned equation becomes: [39]

$$\varepsilon = \frac{\delta i}{i}m\overline{v^2} + m\delta\overline{v^2} \qquad (2)$$

[38] *For Clausius' notation used here see Sec.3 above, or [Clausius, 1871]. The (I) implies that in the following (Ia) there should be $\overline{\delta U}$: but the accurate definition of variation by Clausius is such that it is $\overline{\delta U} = \delta\overline{U}$. An important technical point of Clausius's paper is that it establishes a notion of variation implying that the averages of the variations, in general of little interest because quite arbitrary (the arbitrariness being due, for instance, to possible differences δi in the periods which could lead to differences of order δi depending on the correspondence established between the times of the two motions), coincide with the variations of the averages.*

[39] *Adding $\frac{m}{2}\overline{v^2}$ to both sides.*

The first of these Boltzmann's equations will be identical to my Eq.(I), if the value assigned to ε can be that of my equation. [40]

I cannot agree on this for two reasons.

The first is related to a fact that already Boltzmann casually mentions but, as it seems to me, leaves it aside afterwards, [Clausius, 1872, l.11,p.267]. In his equations both quantities $\overline{\delta v^2}$ and $\delta\overline{v^2}$ (*i.e.* the average value of the variation δv^2 and the variation of the average value of v^2) are fundamentally different from each other, and therefore it happens that his and my equations cannot be confronted.

I have dedicated, in my research, extreme care to avoid leaving variations vaguely defined. And I use a special treatment of the variations by means of the notion of *phase*. This method has the consequence that for every varied quantity the average of the variation is the variation of the average, so that the equations are significantly simple and useful. Therefore I believe that the introduction of such special variations is essential for the subsequent researches, and do not concern a point of minor importance.[41]

If now my variations are inserted in Boltzmann's Eq.(1) the following is deduced:

$$\frac{m}{2}\delta\overline{v^2} = \varepsilon + \overline{X\,\delta x + Y\delta\, y + Z\,\delta Z} \tag{1a}$$

and if next we suppose that the force acting on the point has an ergale [*potential*], which we denote U, the equation becomes $\frac{m}{2}\delta\overline{v^2} = \varepsilon - \delta\overline{U}$, alternatively written as

$$\varepsilon = \frac{m}{2}\delta\overline{v^2} + \delta\overline{U}. \tag{1b}$$

If the value of ε is inserted in Eq.(2) my Eq.(I),(Ia) follow. In spite of the changes in Eq.(1a) and (1b) Boltzmann's equations so obtained are not identical to mine for a second and very relevant reason.

I.e. it is easy to recognize that both Boltzmannian equations and Eq.(1) and (2) hold under certain limiting conditions, which are not necessary for the validity of mine. To make this really evident, we shall instead present the Boltzmannian equations as the most general equations, not subject to any condition. However we shall suppose more conveniently that they take the form taken when the force acting on the point has an ergale [*potential*].

Select, in some way, on the initial trajectory a point as initial point of the motion, which starts at time t_1 as in Boltzmann, and denote the corresponding values of v and U with v_1 and U_1. Then during the entire motion the equation

$$\frac{m}{2}v^2 + U = \frac{m}{2}v_1^2 + U_1 \tag{3}$$

will hold; thus, likewise, we can set for the average values:

[40] *A problem is that in Boltzmann ε appears, at least at first, not clearly defined.*

[41] *The definition of variation in Boltzmann is not really specified until, see p.35, towards the end of the paper. Still Clausius will agree that the variation used by Boltzmann can be properly understood.*

$$\frac{m}{2}\overline{v^2} + \overline{U} = \frac{m}{2}v_1^2 + U_1 \tag{4}$$

About the varied motion suppose that it starts from another point, with another initial velocity and takes place under the action of other forces. Hence we shall suppose that the latter have an ergale $U + \mu V$, where V is some function of the coordinates and μ an infinitesimal constant factor [so $W = 0, \mu V \equiv \delta_e W$ in the notation of Sec.3 above]. Consider now again the two specified points, on the initial trajectory and on the varied one, so instead of v^2 we shall have in the varied motion the value $v^2 + \delta v^2$ and instead of U the value $U + \delta U + \mu(V + \delta V)$; therefore, since $\mu\,\delta V$ is a second order infinitesimal, this can be written $U + \delta U + \mu V$. Hence for the varied motion Eq.(3) becomes:

$$\frac{m}{2}v^2 + \frac{m}{2}\delta v^2 + U + \delta U + \mu V = \frac{m}{2}v_1^2 + \frac{m}{2}\delta v_1^2 + U_1 + \delta U_1 + \mu V_1 \tag{5}$$

so that my calculation of the variation leads to the equation:

$$\frac{m}{2}\overline{v^2} + \frac{m}{2}\delta\overline{v^2} + \overline{U} + \delta\overline{U} + \mu\overline{V} = \frac{m}{2}v_1^2 + \frac{m}{2}\delta v_1^2 + U_1 + \delta U_1 + \mu V_1 \tag{5}$$

Combining the last equation with the Eq.(4) it finally follows

$$\frac{m}{2}\delta v_1^2 + \delta U_1 + \mu(V_1 - \overline{V}) = \frac{m}{2}\delta\overline{v^2} + \delta\overline{U}. \tag{7}$$

This is the equation that in a more general treatment should be in place of the different Boltzmannian Eq.(1b). Thus instead of the Boltzmannian Eq.(2) the following is obtained: [42]

$$\frac{m}{2}\delta v_1^2 + \delta U_1 + \mu(V_1 - \overline{V}) = \frac{\delta i}{i}m\overline{v^2} + m\delta\overline{v}^2. \tag{8}$$

As we see, since such new equations are different from the Boltzmannian ones, we must treat more closely the incorrect quantity ε. As indicated by the found infinitesimal variation of the kinetic energy due to the variation of the motion, it is clear that in the variation ε of the kinetic energy at the initial time one must understand, and hence set:

[42] *Noting that the varied motion will in general have no points in common with the initial motion this is not very clear and might be interpreted as follows. Computing (as done in Sec.3) the variation of the averages to first order, in the following Eq.(8) a first order correction appears instead of $\mu(V_1 - \overline{V})$, due to the change of the external potential by μV (in Sec.3 μV is denoted $\delta_e W$ and, here, it is supposed $W = 0$, which is no loss of generality as noted in Sec.3), equal to $\mu\overline{V}$ which is the external work performed, because of the external forces variation. The Eq.(8) is changed, see Sec.3, into $\delta\overline{K+U} + \mu\overline{V} = \frac{\delta i}{i}m\overline{v^2} + m\delta\overline{v}^2$ which is what is needed, because the l.h.s. can be interpreted as the heat, δQ, that is sent out of the system. This might also clarify the final comment about the vanishing contribution of $\mu(V_1 - \overline{V})$ which, also not very clear, shows that Clausius concludes that Boltzmann's final equations are correct even in presence of external forces; it nevertheless remains that Boltzmann has not considered the external work term: a neglection that he justifies, see previous appendix, convincingly as a matter of simplicity.*

$$\varepsilon = \frac{m}{2}\delta v_1^2.$$

Hence of the three terms, that are to the left in Eq.(7) and (8), the Boltzmannian equations should only contain the first.

Mr. Boltzmann, whose equations incompleteness I have, in my view, briefly illustrated, pretends a wider meaning for ε in his claim to contain at the same time the kinetic energy of the motion and the work, and consequently one could set

$$\varepsilon = \frac{m}{2}\delta v_1^2 + \delta U_1.$$

But I cannot find that this is said anywhere, because in the mentioned places where the work can be read it seems to me that there is a gain that exchanges the kinetic energy with another property of the motion that can transform it into work, which is not in any way understandable, and from this it does not follow that the varied trajectory could be so transformed that is has no point in common with the original while, also, in the transformation the points moved from one trajectory to the other could be moved without spending work.

Hence if one wishes to keep the pretension on the mentioned meaning of ε, then always two of the three terms appearing in Eq.(7) and (8) are obtained, *the third of them, i.e.* $\mu(V_1 - \overline{V})$ *no doubt is missing in his equations.* [43]

On this point he writes: "The term $\mu(\overline{V} - V_1)$ is really missing in my equations, because I have not explicitly mentioned the possibility of the variation of the ergale. Certainly all my equations are so written that they remain correct also in this case. The advantage, about the possibility of considering some small variation of the ergale and therefore to have at hand the second independent variable in the infinitesimal δU exists and from now on it will not be neglected...". [Clausius, 1872, p.271].

I must strongly disagree with the remark in the preceding reply, that all his equations are written so that also in the case in which the ergale varies still remain valid. The above introduced Eq.(1) and (2), even if the quantity ε that appears there receives the extended meaning $\frac{m}{2}\delta v_1^2 + \delta U_1$, are again false in the case in which by the variation of the motion of a point the ergale so changes that the term $\mu(\overline{V}_1 - V)$. has an intrinsic value.[44]

It cannot be said that my Eq.(I) is *implicitly* contained in the Boltzmannian work, but the relevant equations of his work represent, also for what concerns my method of realizing the variations, only a special case of my equations.

Because I must remark that the development of the treatment of the case in which the ergale so changes is not almost unessential, but for researches of this type it is even necessary.

[43] *It seems, however, that the pretension can be reasonably assumed if the (admittedly somewhat obscure) comment in [Boltzmann, 1866, #5,l.-11], which was repeated in [Boltzmann, 1871a, #17,l.12] to prevent Clausius comment, is interpreted properly, while the next comment on* $\mu(\overline{V} - V_1)$ *is about a "gap" already admitted by Boltzmann who essentially said that he did not discuss it for simplicity, see footnote at p.34 above.*

[44] *This is a typo for* $\mu(V_1 - \overline{V})$.

It is in fact possible to consider a body as an aggregate of very many point masses that are under the influence of external and internal forces. The internal forces have an ergale, depending only on the points positions, but in general it stays unchanged in all states of the body; on the contrary this does not hold for the external forces. If for instance the body is subject to a normal pressure p and later its volume v changes by dv, then the external work $p\,dv$ will be performed. This term, when p is varied independently of v, is not an exact differential and the work of the external force cannot, consequently, be representable as the differential of an ergale. The behavior of this force can be so represented: for each given state of the body in which its components are in a state of stationary type it is possible to assign an ergale also to the external forces which, however, does not stay unchanged, unlike that of the internal forces, but it can undergo variations while the body evolves into another state, independent of the change of position of the points.

Keep now in mind the equations posed in the thermology of the changes of state to build their mechanical treatment, which have to be reconsidered to adapt them to the case in which the ergale changes.

I can say that I looked with particular care such generalizations. Hence it would not be appropriate to treat fully the problem, but I obtained in my mechanical equations the above mentioned term $\mu(V_1 - \overline{V})$, for which the corresponding term cannot be found in the mechanical equations. I must now discuss the grounds for this difference and under which conditions such term could vanish. I find that this will be obtained if the ergale variation is not happening instantaneously at a given moment, but gradual and uniform while an entire cycle takes place.[45] And at the same time I claim that the same result is obtained if it is supposed that we do not deal with a single moving point but with *very large numbers of equal points*, all moving in the same way but with different phases, so that at every moment the phases are uniformly distributed and this suffices for each quantity to be evaluated at a point where it assumes a different value thus generating the average value. The latter case arises in the theory of heat, in which the motions, that we call heat, are of a type in which the quantities that are accessible to our senses are generated by many equal points in the same way. Hence the preceding difficulty is solved, but I want to stress that such solution appears well simpler when it is found than when it is searched.[46]

The circumstance that for the motions that we call heat those terms disappear from the averages had as a result that Boltzmann could obtain for the digregation [*free energy*] and the entropy, from his more restricted analysis, results similar to those that I obtained with a more general analysis; but it will be admitted that the real and complete foundation of this solution can only come from the more general treatment.

The validity condition of the result, which remains hidden in the more restricted analyses, will also be evident.

[45] *In other words these are the quasi static transformations, as considered by Boltzmann at the very beginning of his paper.*

[46] *See the footnote before Eq.(8) above.*

In every case Boltzmann restricts attention to motions that take place along closed trajectories. Here we shall consider motions on non closed curves, hence it now becomes necessary a special argument.[47]

Here too I took a different approach with respect to Boltzmann, and this is the first of the two points mentioned above, in which Boltzmann's result on disgregation and entropy differ. In his method taking into account of time is of the type that I called *characteristic time of the period of a motion*, essentially different. The second point of difference is found in the way in which we defined temperature. The special role of these differences should be followed here in detail, but I stop here hoping to come back to it elsewhere.[48]

Finally it will not be superfluous to remark that in another of my published works the theorem whereby in every stationary motion *the average kinetic energy equals the virial* remains entirely outside of the priority question treated here. This theorem, as far as I know, has not been formulated by anyone before me.

C Collision analysis and equipartition

Quotes and comments on: *Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten*, 1868, [Boltzmann, 1868a, #5,p.49-96].

All principles of analytic mechanics developed so far are limited to the transformation of a system of point masses from a state to another, according to the evolution laws of position and velocity when they are left in a motion unperturbed for a long time and are concerned, with rare exceptions, with theorems of the ideal, or almost ideal, gas. This might be the main reason why the theorems of the mechanical theory of heat which deal with the motions so far considered are so uncorrelated and defective. In the following I shall treat several similar examples and finally I shall establish a general theorem on the probability that the considered point masses occupy distinct locations and velocities. [49]

I. The case of an infinite number of point masses

Suppose we have an infinite number of elastic spheres of equal mass and size and constrained to keep the center on a plane. A similar more general problem has been solved by Maxwell (Phil.Mag., March 1868);[50] however partly because of the non complete exposition partly also because the exposition of Maxwell in its broad lines is difficult to understand, and because of a typo (in formulae (2) and (21) on the quantities called dV^2 and dV) will make it even more difficult, I shall treat here the problem again from the beginning.

[47] *The case of motions taking place on non closed trajectories is, however, treated by Boltzmann.*

[48] While this article was in print I found in a parallel research that the doubtful expression, to be correct in general, requires a change that would make it even more different from the Boltzmannian one.

[49] *It will be what today is called microcanonical distribution.*

[50] *This could be [Maxwell, 1866, 1866].*

It is by itself clear that in this case every point of the plane is a possibly occupied location of the center of one of the elastic spheres and every direction has equal probability, and it remains to determine the speeds. Let $\varphi(c)dc$ be the sum of the time intervals during which the speed of one of the spheres happens to have a value between c and $c+dc$ divided by a very large total time: which is also the probability that c is between c and $c+dc$ and let there be N spheres per unit area, then

$$N\,\varphi(c)\,dc$$

denotes the number of spheres whose center is within the unit of surface where the velocities are between c and $c+dc$.[51]

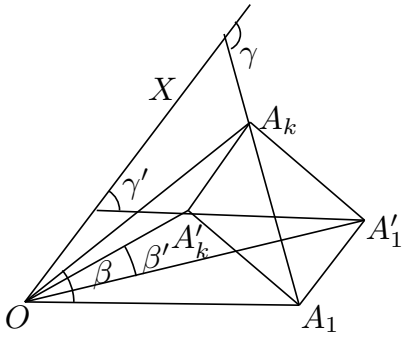

fig.2

.

Consider now a sphere, that I call I, with speed c_1 towards OA_1, Fig.1, represented in size and direction, and let OX the line joining the centers at the impact moment and let β be the angle between the velocities c_1 and c_k, so that the velocities components of the two spheres orthogonal to OX stay unchanged, while the ones parallel to OX will simply be interchanged, as the masses are equal; hence let us determine the velocities before the collision and let A_1A_1' be parallel to OX and let us build the rectangle $A_1A_1'A_kA_k'$; OA_1' and OA_k' be the new velocities and β' their new angle. Consider now the two diagonals of the rectangle A_1A_k and $A_1'A_k'$ which give the relative velocities of the two spheres, g before and g' after the collision, and call γ the angle between the lines A_1A_k and OX, and γ' that between the lines $A_1'A_k'$ and OX; so it is easily found: .....

[*A* **long** *analysis follows about the relation between the area elements* $d^2\mathbf{c}_1d^2\mathbf{c}_k$ *and the corresponding* $d^2\mathbf{c}_1'd^2\mathbf{c}_k'$. *Collisions occur with the collision direction and the line connecting the centers forming an angle, between* β *and* $\beta+d\beta$ *with probability proportional to* $\sigma(\beta)d\beta$ *where* $\sigma(\beta)$ *is the cross section (equal to* $\sigma(\beta)=\frac{1}{2}r\sin\beta$ *in the case, studied here, of disks of radius* r*). Then the density* $f(\mathbf{c})d^2\mathbf{c}$ *must have the property* $\varphi(\mathbf{c}_1)f(\mathbf{c}_k)\sigma(\beta)d\beta=\varphi(\mathbf{c}_1')f(\mathbf{c}_k')\,\sigma(\pi-\beta)d\beta\cdot J$ *where* J *is the ratio* $\frac{d^2\mathbf{c}_1'd^2\mathbf{c}_k'}{d^2\mathbf{c}_1d^2\mathbf{c}_k}$, *if the momentum and kinetic energy conservation relations hold:* $\mathbf{c}_1+\mathbf{c}_k=\mathbf{c}_1'+\mathbf{c}_k'$ *and* $\mathbf{c}_1^2+\mathbf{c}_k^2=\mathbf{c}_1^{'2}+\mathbf{c}_k^{'2}$ *and if the angle between* $\mathbf{c}_1-\mathbf{c}_k$ *and* $\mathbf{c}_k'-\mathbf{c}_1'$ *is* β.

[51] *So the probability of speed in dc is the fraction of time spentby the particles with speed in dc.*

The analysis leads to the conclusion, well known, that $J = 1$; therefore it must be $f(\mathbf{c}_1)f(\mathbf{c}_k) = f(\mathbf{c}'_1)f(\mathbf{c}'_k)$ for all four velocities that satisfy the conservation laws of momentum and energy: this implies that $f(\mathbf{c}) = const\, e^{-hc^2}$. Boltzmann uses always the directional uniformity supposing $f(\mathbf{c}) = \varphi(c)$ and therefore expresses the probability that the modulus of the velocity is between c and $c + dc$ as $\varphi(c)cdc$, hence (keeping in mind that the 2-dimensional case is considered so that $\int_0^\infty f(c)cdc = 1$) the result is expressed by $\varphi(c) = b\, e^{-hc^2}$, with $b = 2h$ a normalization constant.
In reality if systematic account was taken of the volume preserving property of canonical transformations (i.e. to have Jacobian 1) the strictly algebraic part of evaluating the Jacobian, would save several pages of the paper. It is interesting that Boltzmann had to proceed to rediscover this very special case of a general property of Hamiltonian mechanics.
Having established this result for planar systems of elastic disks (the analysis has been very verbose and complicated and Boltzmann admits that "Maxwell's argument was simpler", but he says to have chosen on purpose a direct approach based on "very simple examples", [Boltzmann, 1868a, #5,p.58]), Boltzmann considers a 3–dimensional case with an interaction which is more general than elastic collision between rigid spheres, and admits that it is described by a potential $\chi(r)$, with very short range. However he says that, since Maxwell has treated completely the problems analogous to the ones just treated in the planar case, he will study a new problem in subsection 2. Namely the one dimensional problem of a ball M moving on a line on which move also hard point particles m: M is subject to a central force of potential $\chi(x)$ towards a fixed center O and the particles m can collide with M but, a long time having elapsed, their system has acquired a stationary velocity distribution $\varphi(c)dc$. The aim is to determine the distribution of position x and speed C of the particle M and to show that is generalizes the hard balls Maxwellian into $2Be^{-h(\frac{C^2}{2M} - \chi(x))}dCdx$ and obtain that the other balls have a Maxwellian velocity distribution, $\varphi(c)$ proportional to $e^{-h\frac{c^2}{2m}}$, with h the inverse temperature.]

I.2. (p.61)

Along a line OX an elastic ball of mass M is moving attracted by O by a force depending only on the distance. Against O are moving other elastic balls of mass m and their diverse velocities during disordered time intervals dart along the same line, so that if one considers that all flying balls have run towards O long enough on the line OX without interfering with each other, the number of balls with velocity between c and $c + dc$, which in average are found in the unit length, is a given function of c, *i.e.* $N\varphi(c)dc$.

The potential of the force, which attracts M towards O be $\chi(x)$, hence as long as the motion [of M] does not encounter collisions it will be

$$\frac{MC^2}{2} = \chi(x) + A \tag{9}$$

where C is the speed of the ball M and x the distance between its center and

O. Through the three quantities x, A and c the kind of collision is fixed....

[*The discussion continues and the conclusion is that the joint distribution of* x, C, c *for finding the particle* M *within* dx *with speed in* dC *and a particle* m *with speed in* dc *is the canonical distribution* $Be^{-h(\frac{M}{2}C^2-\chi(x))-h\frac{m}{2}c^2}dxdCdc$. *It has to be kept in mind that only events on the line* OX *are considered so that the problem is* 1*–dimensional. The argument builds a kind of Boltzmann's equation (like the analysis in subsection 1) very much resembling Maxwell's treatment in [Maxwell, 1866] and is a precursor of the later development of the Boltzmann's equation, [Boltzmann, 1872, #22], and follows the same path. The analysis, here and in the similar but increasingly complex problems in the rest of Section II, will reveal itself very useful to Boltzmann in the other two papers of the 1871 "trilogy", and eventually in the 1872 construction of the Boltzmann's equation, because it contains all technical details to be put together to derive it.*
The 3*-dimensional corresponding problem is treated in Sec.I, subsection 3 (p.64). In Sec.I subsection 4 (p.70) all points are again on a line and the interaction between the particle* M *(now called* I*) with a fixed center at* O *is as in subsection 2, but the interaction between the* m *point particles (now called* II*) and* M *is no longer hard core but is governed by a potential with finite range* ℓ. *It is supposed that the fraction of time the point II has speed between* c *and* $c + dc$ *(the problem is again* 1*-dimensional) is* $N\varphi(c)dc$ *and that events in which two or more particles II come within* ℓ *of* I *can be neglected. The analysis leads to the "same" results of subsections 2 and 3 respectively for the* 1 *and* 3 *dimensional cases.*
In Sec.I subsection 5 (p.73) a similar problem is studied: the particle I *and the particles* II *move in space rather than on a line. It is more involved as the angular momentum also enters into the equations. Again the results are as expected.*
The problems of increasing complexity are shown to admit solutions that can be viewed to fit in a general context that unifies them. The purpose is to consider simple cases in which, however, not all interactions are hard core interactions and softer potentials are treated.
The series of examples in Sec.I prepares for the main part of the paper where Boltzmann solves the general problem of the equilibrium distribution of a system of interacting particles, discovering the microcanonical distribution. The technical preparation is presented in Sec.II (see below) where, still assuming that the interaction between the particles is very short range, the Maxwell distribution for the velocities is derived for the first time via a combinatorial argument in a discretized representation of phase space, implicitly assuming that all microscopic configurations are visited during an equal fraction of time.]

II. On the equipartition of the kinetic energy for a finite number of point masses (p.80)

[*In this section finitely many particles confined in a bounded container are studied in various (stationary) cases, evaluating the finite volume corrections and*

showing that equipartition of kinetic energies always holds exactly. The first case, in subsection II.6, deals with a planar case. Here the distribution of kinetic energy in shells $k_i, k_i + dk_i$ (with $k_i = i\frac{1}{p}$ integer multiple of a small quantity $\frac{1}{p}$) is determined to be uniform (under the constraint of fixed total kinetic energy, of the n particles, at $n\kappa$), p.83. This is used to determine the fraction of time the energy of a particle is in the shell between k and $k + dk$; determined by the combinatorial count of the number of ways the total kinetic energy can be split in the various shells and assuming such number proportional to the fraction of time spent in the shell; i.e. the fraction of time in which the energy is in the shell dk equals the average number of particles with energy in dk: a forerunner of the ergodic hypotesis. The arguments are as follows:]

In a very large area, bounded in every direction, let there be n point masses, of masses $m_1, m_2, \ldots, m_n$ and velocities $c_1, c_2, \ldots, c_n$, and between them act arbitrary forces, which *just begin to act at a distance which vanishes compared to their mean distance* [*italics added*].[52] Naturally all directions in the plane are equally probable for such velocities. But the probability that the velocity of a point be within assigned limits and likewise that the velocity of the others be within other limits, will certainly not be the product of the single probabilities; the others will mainly depend on the value chosen for the velocity of the first point. The velocity of the last point depends from that of the other $n - 1$, because the entire system must have a constant amount of kinetic energy.

I shall identify the fraction of time during which the velocities are so partitioned that c_2 is between c_2 and $c_2 + dc_2$, likewise c_3 is between c_3 and $c_3 + dc_3$ and so on until c_n, with the probability $\varphi_1(c_2, c_3, \ldots, c_n)dc_2\, dc_3 \ldots dc_n$ for this velocity configuration.

The probability that c_1 is between c_1 and $c_1 + dc_1$ and the corresponding velocities different from c_2 are between analogous limits be $\varphi_2(c_1, c_3, \ldots, c_n)\cdot dc_1\, dc_3 \ldots dc_n$, *etc.*.

Furthermore let

$$\frac{m_1c_1^2}{2} = k_1,\ \frac{m_2c_2^2}{2} = k_2,\ \ldots\ \frac{m_nc_n^2}{2} = k_n$$

be the kinetic energies and let the probability that k_2 is between k_2 and k_2+dk_2, k_3 is between k_3 and $k_3 + dk_3$ ... until k_n be $\psi_1(k_2, k_3, \ldots, k_n)\, dk_2\ dk_3 \ldots dk_n$. And analogously define $\psi_2(k_1, k_3, \ldots, k_n)\, dk_1\, dk_3 \ldots dk_n$ *etc.* ., so that

$$m_2c_2 \cdot m_3c_3 \ldots m_nc_n\, \psi_1(\frac{m_2c_2^2}{2}, \frac{m_3c_1^3}{2}, \ldots, \frac{m_nc_n^2}{2}) = \varphi_1(c_2, c_3, \ldots, c_n) \quad \text{or}$$
$$\varphi_1(c_2, c_3, \ldots, c_n) = 2^{\frac{n-1}{2}}\, \sqrt{m_2m_3 \ldots m_n}\, \sqrt{k_2k_3 \ldots k_n}\, \psi_1(k_2, k_3, \ldots, k_n)$$

and similarly for the remaining φ and ψ.

Consider a collision involving a pair of points, for instance m_r and m_s, which is such that c_r is between c_r and $c_r + dc_r$, and c_s is between c_s and $c_s + dc_s$. Let

[52] *This assumption is meant to allow still neglecting the interaction time and consider collisions instantaneous so that the total kinetic energy is conserved.*

the limit values of these quantities after the collision be between c'_r and $c'_r + dc'_r$ and c'_s be between c'_s and $c'_s + dc'_s$.

It is now clear that the balance of the kinetic energy will remain valid always in the same way when many point, alternatively, come into collision and are moved within different limits, as well as the other quantities whose limits then can be remixed, among which there are the velocities of the remaining points.

The number of points that are between assigned limits of the velocities, which therefore have velocities between c_2 and $c_2 + dc_2 \ldots$, are different from those of the preceding problems because instead of the product $\varphi(c_r)dc_r\varphi(c_s)dc_s$ appears the function $\varphi_1(c_2, c_3, \ldots, c_n)dc_2\, dc_3 \ldots\, dc_n$. This implies that instead of the condition previously found

$$\frac{\varphi(c_r) \cdot \varphi(c_s)}{c_r \cdot c_s} = \frac{\varphi(c'_r) \cdot \varphi(c'_s)}{c'_r \cdot c'_s}$$

the new condition is found:

$$\frac{\varphi_1(c_2, c_3, \ldots, c_n)}{c_r \cdot c_s} = \frac{\varphi_1(c_2, \ldots, c'_r, \ldots, c'_s, \ldots, c_n)}{c'_r \cdot c'_s}$$

The same holds, of course, for $\varphi_2, \varphi_3, \ldots$. If the function φ is replaced by ψ it is found, equally,

$$\psi_1(k_2, k_3, \ldots, k_n) = \psi_1(k_2, k_3, \ldots, k'_r, \ldots, k'_s, \ldots, k_n), \qquad \text{if } k_r + k_s = k'_r + k'_s.$$

Subtract the differential of the first of the above relations $\frac{d\psi_1}{dk_r}dk_r + \frac{d\psi_1}{dk_s}dk_s = \frac{d\psi_1}{dk'_r}dk'_r + \frac{d\psi_1}{dk'_s}dk'_s$ that of the second $[dk_r + dk_s = dk'_r + dk'_s]$ multiplied by λ and set equal to zero the coefficient of each differential, so that it is found:

$$\lambda = \frac{d\psi_1}{dk_r} = \frac{d\psi_1}{dk_s} = \frac{d\psi_1}{dk'_r} = \frac{d\psi_1}{dk'_s}.$$

I.e., in general, $\frac{d\psi_1}{dk_2} = \frac{d\psi_1}{dk_3} = \frac{d\psi_1}{dk_4} = \ldots \frac{d\psi_1}{dk_n}$, hence ψ_1 is function of $k_2 + \ldots + k_n$. Therefore we shall write $\psi_1(k_2, \ldots, k_n)$ in the form $\psi_1(k_2 + k_3 + \ldots + k_n)$. We must now find the meaning of the equilibrium between m_1 and the other points. And we shall determine the full ψ_1.

It is obtained simply with the help of the preceding ψ of which of course the ψ_1 must be a sum. But these are all in reciprocal relations. If in fact the total kinetic energy of the system is $n\kappa$, it is

$$k_1 + k_2 + \ldots + k_n = n\kappa$$

It follows that $\psi_1(k_2 + k_3 + \ldots + k_n)dk_2dk_3 \ldots dk_n$ can be expressed in the new variables[53]

$$k_3, k_4, \ldots, n\kappa - k_1 - k_3 - \ldots - k_n = k_2$$

[53] *In the formula k_2 and k_1 are interchanged.*

and so it must be for $\psi_2(k_1 + k_3 + \ldots + k_n)dk_1dk_3 \ldots dk_n$. Hence $\psi_1(k_2 + k_3 + \ldots + k_n)$ can be converted in $\psi_1(n\kappa - k_1)$ and $dk_2dk_3 \ldots dk_n$ in $dk_1dk_3 \ldots dk_n$. Hence also

$$\psi_1(n\kappa - k_1) = \psi_2(k_1 + k_3 + \ldots + k_n) = \psi_2(n\kappa - k_2)$$

for all k_1 and k_2, therefore all the ψ are equal to the same constant h. This is also the probability that in equal time intervals it is k_1 between k_1 and $k_1 + dk_1$, k_2 is between k_2 and $k_2 + dk_2$ *etc.* , thus for a suitable h, it is $h\, dk_1\, dk_2\, \ldots\, dk_n$ were again the selected differential element must be absent. Of course this probability that at a given instant $k_1 + k_2 + k_3 + \ldots$ differs from $n\kappa$ is immediately zero.

The probability that c_2 is between c_2 and $c_2 + dc_2$, c_3 between c_3 and $c_3 + dc_3 \ldots$ is given by

$$\varphi_1(c_2, c_3, \ldots, c_n)\, dc_2\, dc_3\, \ldots\, dc_n = m_2m_3 \ldots m_n \cdot h \cdot c_2c_3 \ldots c_ndc_2\, dc_3\, \ldots\, dc_n.$$

Therefore the point c_2 is in an annulus of area $2\pi c_2dc_2$, the point c_3 in one of area $2\pi c_3dc_3$ *etc.* , that of c_1 on the boundary of length $2\pi c_1$ of a disk and all points have equal probability of being in such annuli.

Thus we can say: the probability that the point c_2 is inside the area $d\sigma_2$, the point c_3 in $d\sigma_3$ *etc.* , while c_1 is on a line element $d\omega_1$, is proportional to the product

$$\frac{1}{c_1}\, d\omega_1\, d\sigma_2\, d\sigma_3\, \ldots\, d\sigma_n,$$

if the mentioned locations and velocities, while obeying the principle of conservation of the kinetic energy, are not impossible.

We must now determine the fraction of time during which the kinetic energy of a point is between given limits k_1 and $k_1 + dk_1$, without considering the kinetic energy of the other points. For this purpose subdivide the entire kinetic energy in infinitely small equal parts (p), so that if now we have two point masses, for $n = 2$ the probability that k_1 is in one of the p intervals $[0, \frac{2\kappa}{p}]$, $[\frac{2\kappa}{p}, \frac{4\kappa}{p}]$, $[\frac{4\kappa}{p}, \frac{6\kappa}{p}]$ *etc.* is equal and the problem is solved.

For $n = 3$ if k_1 is in $[(p-1)\frac{3\kappa}{p}, p\frac{3\kappa}{p}]$, then k_2 and k_3 must be in the interior of the p intervals. If k_1 is in the next to the last interval, *i.e.* if

$$(p-2)\frac{3\kappa}{p} \leq k_1 \leq (p-1)\frac{3\kappa}{p}$$

two cases are possible ....

[*Follows the combinatorial calculation of the number of ways to obtain the sum of n multiples* $p_1, \ldots, p_n$ *of a unit* ε *and* $p_1\varepsilon = k_1$ *such that* $\sum_{i=2}^{n-1} p_i\varepsilon = n\kappa - p_1\varepsilon$, *and Boltzmann chooses* $\varepsilon = \frac{\kappa}{p}$ *with* p *"infinitely large": i.e.*

$$\sum_{p_2=0}^{n\kappa/\varepsilon - p_1} \quad \sum_{p_3=0}^{n\kappa/\varepsilon - p_1 - p_2} \quad \ldots\ldots \quad \sum_{p_{n-1}=0}^{n\kappa/\varepsilon - p_1 - \ldots - p_{n-2}} 1$$

the result is obtained by explicitly treating the cases $n = 2$ and $n = 3$ and inferring the general result in the limit in which $\varepsilon \to 0$.
The ratio between this number and the same sum performed also on p_1 is, fixing $p_1 \in [k_1/\varepsilon, (k_1 + dk_1)/\varepsilon]$,

$$\frac{dk_1 \int_0^{n\kappa-k_1} dk_2 \int_0^{n\kappa-k_1-k_2} dk_3 \ \ldots \int_0^{n\kappa-k_1-k_2-\ldots-k_{n-2}} dk_{n-1}}{\int_0^{n\kappa} dk_1 \int_0^{n\kappa-1} dk_2 \int_0^{n\kappa-k_1-k_2} dk_3 \ \ldots \int_0^{n\kappa-k_1-k_2-\ldots-k_{n-2}} dk_{n-1}}$$
$$= \frac{(n-1)(n\kappa-k_1)^{n-2} dk_1}{(n\kappa)^{n-1}},$$

This is, however, remarked after the explicit combinatorial analysis of the cases $n = 2$ and $n = 3$ from which the last equality is inferred in general (for $\varepsilon \to 0$). Hence the "remark" is in reality a proof simpler than the combinatorial analysis of the number of ways to decompose the total energy as sum of infinitesimal energies. The choice of Boltzmann is a sign of his preference for arguments based on a discrete view of physical quantities. And as remarked in [Bach, 1990] this remains, whatever interpretation is given to it, an important analysis.
In the successive limit, $n \to \infty$, the Maxwell's distribution (in dimension 2) is obtained.

$$\frac{1}{\kappa} e^{-k_1/\kappa} dk_1$$

concluding the argument.

In the next subsection II.7 (p.86) Boltzmann repeats the analysis in the 3-dimensional case obtaining again the Maxwellian distribution for the speed of a single particle in a system of n point masses in a finite container with perfectly elastic walls, not necessarily flat. Particles interact only if closer that their average distance and so close that the total kinetic energy can be considered constant.
Finally in Sec. II.8 the case is considered in which N particles interact as in Sec. II.7 and with n other particles which do not interact with each other but do interact with the first N; again the interaction range is so short that collisions can be considered instantaneous, as assumed at the beginning of Sec. II.
Then the final (surprising and original) solution to the general problem is in Sec.III (see below) where 'no assumption', see the comment by Maxwell at p.49 below, is made on the density of particles and on the interaction potential to compute the probability of microscopic configurations.]

III. General solution of the kinetic energy equipartition problem

[*The section III, p.92, is remarkable for the generality, for the derivation of the microcanonical distribution and for the implicit emergence of the Ergodic Hypothesis, as commented in [Maxwell, 1879]:*

"The only assumption which is necessary for the direct proof is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy. Now it is manifest

that there are cases in which this does not take place. The motion of a system not acted on by external forces satisfies six equations besides the equation of energy, so that the system cannot pass through those phases, which, though they satisfy the equation of energy, do not also satisfy these six equations. Again, there may be particular laws of force, as for instance that according to which the stress between two particles is proportional to the distance between them, for which the whole motion repeats itself after a finite time. In such cases a particular value of one variable corresponds to a particular value of each of the other variables, so that phases formed by sets of values of the variables which do not correspond cannot occur, though they may satisfy the seven general equations. But if we suppose that the material particles, or some of them, occasionally encounter a fixed obstacle such as the sides of a vessel containing the particles, then, except for special forms of the surface of this obstacle, each encounter will introduce a disturbance into the motion of the system, so that it will pass from one undisturbed path into another. The two paths must both satisfy the equation of energy, and they must intersect each other in the phase for which the conditions of encounter with the fixed obstacle are satisfied, but they are not subject to the equations of momentum. It is difficult in a case of such extreme complexity to arrive at a thoroughly satisfactory conclusion, 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.

Remark: Here the particles interact with a rather general force, no restriction to its range. Furthermore the microscopic configurations are counted via the occupation number of shells in kinetic energy and in cubic boxes in position space. However the shells in kinetic energy space are measured in terms of the speed and are appropriately given the weight c^2dc or $\sqrt{k}dk$ which would amounts to imagine the shell covered by cubic boxes in the velocity space. Then the distribution of both velocity and positions is counted simply using the combinatorial study of the previous section: the result is a uniform distribution under the condition that the amount of kinetic energy of a microscopic configuration located in a cubic ($3n$-dimensional) box centered at a point $x \in R^{3n}$ is $n\kappa - \chi(x)$ (p.95,l.25): the result, p.95,l.31 and following, would be called today a microcanonical distribution, and Boltzmann integrates it over all momenta but one, to obtain the equipartition theorem. The following arguments are given:]

Consider n points-mass given in space with masses $m_1, \ldots, m_n$. Let their interaction be between pairs and arbitrarily depending on the reciprocal distance. Also arbitrary forces with arbitrary fixed centers (points with infinite mass) can act. The forces by which every point will be affected are subject to the condition of depending on the position and of admitting a potential. In all systems the total energy, still denoted $n\kappa$ (as in the preceding sections was instead denoted the kinetic energy), is assigned; we ask the probability that each point can be found in a given place with its velocity having a given value. We denote the positions of the point m_1 by three rectilinear coordinates

x_1, y_1, z_1, of the point m_2 by x_2, y_2, z_2, *etc.* , and the three components of the velocity c_1 of the point m_1 with the three coordinates u_1, v_1, w_1 and those of the point m_2 with u_1, v_2, w_2, *etc.* . Denote the time spent with x_1 in the interval $x_1, x_1 + dx_1$, y_1 in $y_1, y_1 + dy_1$ and z_1 in $z_1 + dz_1$ and also m_1 in the volume element $dx_1 dy_1 dz_1$, and likewise for the point m_2 .....and the velocities ... u_1 in $u_1 + d_1$, v_1 in $v_1, v_1 + dv_1$, w_1 in $w_1, w_1 + w_1$, ... c_1 in $d\sigma_1 = du_1 dv_1 dw_1$, ... , c_{n-1} in $d\sigma_{n-1} = d\sigma_{n-1} = du_{n-1} dv_{n-1} dw_{n-1}$, and finally the c_n in the surface element $d\omega_n$. [54] Divide the length of these time intervals by the total time elapsed obtaining:

$$f(x_1, y_1, z_1, \ldots, u_1, v_1, w_1, \ldots) dx_1 dy_1 dz_1 \cdots du_1 dv_1 dw_1 \cdots du_n dv_n d\omega_n$$

[*The analysis continues and yields a long derivation of the formula that in modern notations would be that the probability of a phase space volume element* $d^{3n}pd^{3n}q$ *for a system with total energy* $n\kappa$ *is proportional to*

$$\delta(\frac{1}{2m}p^2 + \chi(q) - n\kappa) d^{3n}pd^{3n}q$$

and the number of particles with position in $d^{3n}q$*, or* $ds_1 \ldots ds_n$ *in Boltzmann's notation, is (integrating over the momenta) obtained from the probability that the* n *particles are in the volume elements* $ds_1, \ldots, ds_n$*). It is proportional to:*

$$(n\kappa - \chi(q))^{\frac{3n-2}{2}} ds_1 \ldots ds_n$$

i.e. it is the microcanonical ensemble distribution of the velocities (Maxwellian in the velocities for large $n\kappa$*). The analysis of the earlier sections was carried, taking* $\chi \sim 0$ *to keep conserved the kinetic energy (aside from a neglegible fraction of time) and under a form of the ergodic hypothesis (saying that the system spends equal time in equal phase space volumes): it implied equipartition of kinetic energy. The last section analysis is a strong extension of all the previous sections results and yields equipartition in presence of a rather arbitrary interaction potential and even the microcanonical distribution. He also remarks that positions and velocities that would seem permitted, because* $n\kappa > \chi(q)$*, may not be such if the domain where* $n\kappa > \chi(q)$ *is not connected.*
As noted above (see the remark, p.50) on the implicit split of the momentum shell $c, c + dc$ *equal cells in number proportional to* $c^2 dc$*) the discretisation used can be thought as done by dividing phase space in small parallelepipedal cells (in the* $6n$*-dimensional phase space): this is an essential point. Boltzmann does not comment on that: but he wants to think, as he said, later but repeatedly, since he started realizing that his ideas were misunderstood, that derivatives and integrals are just "approximations" of certain ratios or of certain sums. See more detailed comments at p.20 above. The highlight of the work, and its conclusion, is:*]

p.96. As special case from the first theorem it follows, as already remarked in my paper on the mechanical interpretation of the second theorem, that the

[54] *the last velocity is determined by its direction, because the total energy is fixed to* $n\kappa$*.*

kinetic energy of an atom in a gas is equal to that of the progressive motion of the molecule.[55] The latter demonstration also contains the solution of others that were left incomplete: it tells us that for such velocity distributions the balance of the kinetic energies is realized in a way that could not take place otherwise.

An exception to this arises when the variables $x_1, y_1, z_1, x_2, \ldots, v_n$ are not independent of each other. This can be the case of all systems of points in which the variables have special values, which are constrained by assigned relations that remain unaltered in the motions, but which under perturbations can be destroyed (labile equipartition of kinetic energy), for instance when all points and the fixed centers are located on a mathematically exact line or plane. A stable balance is not possible in this case, when the points of the system are so assigned that the variables for all initial data within a certain period come back to the initial values, without having consequently taken all values compatible with the energy conservation.[56]

Therefore such way of achieving balance is always so infinitely more possible that immediately the system ends up in the set of domains discussed above when, for instance, a perturbation acts on a system of points which evolves within a container with elastic walls or, also, on an atom in free motion which collides against elastic walls.[57]

[*Boltzmann identifies the probability of visiting a cell in the full phase space with the fraction of time spent in it by the phase space point discretized on a regular lattice. Being interested in the equipartition integrates over the momenta: not using the delta function, as it would be done today, his argument becomes somewhat involved.*
In [Bach, 1990] the question is raised on whether Boltzmann would have discovered the Bose-Einstein distribution before Planck referring to the way he employs the discrete approach to compute the number of ways to distribute kinetic energy among the various particles, after fixing the value of that of one particle, in [Boltzmann, 1868a, #5,p.84,85]. This is an interesting and argumented view, however Boltzmann considered here the discrete view a "fiction", see also [Boltzmann, 1877b, #42,p.167], and the way the computation is done would not distinguish whether particles were considered distinguishable or not: the limiting case of interest would be the same in both cases (while it would be quite different if the continuum limit was not taken, leading to a Bose-Einstein like distribution, see [Gallavotti, 2000]). This may have prevented him to be led to the extreme consequence of considering the difference physically significant and to compare the predictions with those that follow in the continuum

[55] *to which the atom belongs*

[56] *This last paragraph refers to possible lack of equipartition in cases in which the system admits constants of motion due to symmetries that are not generic and therefore are destroyed by "any" perturbation (like the harmonic chains).*

[57] [Editorial comment added to the Wissenshaftliche version of the paper] This last paragraph is questionable. It is not proved that despite reflexions against elastic walls or despite the action of a single atom modifying the kinetic energy equations, or other integrals, the system may not go through all compatible values.

limit with the distribution found with distinguishable particles, discussed later in [Boltzmann, 1877b, #42], see also [Gallavotti, 2000, Sec.(2.2),(2.6)].]

D Density in phase space: example

Comments on: *Lösung eines mechanisches Problems*, 1868, [Boltzmann, 1868b, #6,p.97-105].

[*An example about the general theory of Sec.III of [Boltzmann, 1868a, #5] is attempted here. The aim of the example it to exhibit a simple case in which the difficult problem of finding the region of phase space visited by a trajectory is the set of all configurations with a given energy so that, on the basis of the previous work, the probability of finding a point mass occupying a given position with given velocity can be solved and shown to be given by equidistribution (i.e. microcanonical).*]
Boltzmann considers the simple system consisting in a point mass [mass $= 1$*] subject to a central gravitational force with potential* $-\frac{\alpha}{2R}$ *and to a centrifugal barrier augmented by a potential* $+\frac{\beta}{2R^2}$*: furthermore the point mass is reflected by an obstacle consisting in a straight line, e.g.* $y = \gamma > 0$*.*]

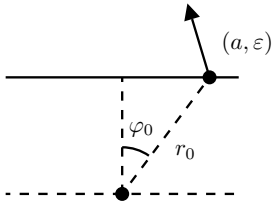

fig.3

.

The discussion is an interesting example of a problem in ergodic theory for a two variables map, "not really easy to find" as a soluble case among the great variety of cases. Angular momentum $-a$ *is conserved between collisions and the motion is explicitly reducible to an elementary quadrature which (here* $r \equiv R$ *and* A *is a constant of motion equal to twice the total energy, constant because collisions with the line are supposed elastic) yields a function:*

$$F(r, a, A) \stackrel{def}{=} \frac{a}{\sqrt{a^2+\beta}} \arccos\left(\frac{2(a^2+\beta)/r - \alpha}{\sqrt{\alpha^2 + 4A(a^2+\beta)}}\right)$$

such that the polar angle at time t *is* $\varphi(t) - \varphi(0) = F(r(t), a_0, A) - F(r(0), a_0, A)$*. Let* $\varepsilon_0 \stackrel{def}{=} \varphi(0) - F(r(0), a_0, A)$*, then if* φ_0, a_0 *are the initial polar angle and the angular momentum of a motion that comes out of a collision at time* 0 *then* $r(0)\cos\varphi_0 = \gamma$ *and* $\varphi(t) - \varepsilon_0 = F(r(t), a_0, A)$ *until the next collision. Which will take place when* $\varphi_1 - \varepsilon_0 = F(\frac{\gamma}{\cos\varphi_1}, a_0, A)$ *and if* a_1 *is the outgoing angular momentum from then on* $\varphi(t) - \varepsilon_1 = F(r(t), a_1, A)$ *with* $\varepsilon_1 \stackrel{def}{=} \varphi_1 - F(\frac{\gamma}{\cos\varphi_1}, a_1, A)$*. Everything being explicit Boltzmann computes the Jacobian of the just defined map* $S : (a_0, \varepsilon_0) \to (a_1, \varepsilon_1)$ *and shows that it is* 1 *(which is carefully checked without reference to the canonicity of the map). The map is supposed to exist,*

i.e. that the Poincaré's section defined by the timing event "hit of the fixed line" is transverse to the solution flow (which may be not true: if $A \geq 0$ or, even if $A < 0$, unless γ is small enough).
Hence the observations timed at the collisions, i.e. the evolution of the values a, ε at the successive collisions, admit an invariant measure $d\varepsilon da$. If the allowed values of a, ε vary in a bounded set (which certainly happens if $A < 0$) the measure $\frac{d\varepsilon da}{\int d\varepsilon da}$ is an invariant probability measure, i.e. the microcanonical distribution, which can be used to compute averages and frequency of visits to the points of the plane ε, a.
The interest of Boltzmann in the example was to show that, unless the interaction was very special (e.g. $\beta = 0$), the motion would invade the whole energy surface so that the stationary probability distribution would be positive on the entire phase space, in essential agreement with the idea of ergodicity (of the earlier work, see Appendix C).
However the stationary distribution that is studied is just one invariant distribution: Boltzmann did not yet suspect that there might be other invariant distributions. The doubt will arise in his mind soon: as he will point out that other invariant distributions might exist (even if described by a density in phase space), [Boltzmann, 1871b, #18,p.255] and AppendixE below, and he will be troubled by the problem.
Boltzmann proves that the map $(a, \varepsilon) \to (a', \varepsilon')$, of the data of a collision to those of the next, has Jacobian 1.[58] *From this he infers that the frequency of visit to a rectangle $da\, d\varepsilon$ is a constant function of (a, ε) and actually he claims that a stationary distribution of the successive values of (a, ε) is, therefore, uniform in the set in which a, ε vary. And he then uses the distribution to derive its form in other variables and to evaluate various averages. A related, very simplified, version is in Sec.5 above. See also [Boltzmann, 1877a, #39].*
The conclusion, [Boltzmann, 1868a, #6,p.102], is however somewhat fast: because he is assuming that the invariant distribution has a density in a, ε and that it is the only distribution with a density (and furthermore, strictly speaking, that the distribution is ergodic in the modern sense of the notion). See Fig.4. for a simple heuristic test of density in the above case and in a second simple case (Boltzmann concludes the paper by briefly discussing even more general cases). [59]

[58] *The analysis is long and detailed: in modern language it could be carried by remarking that the action angle coordinates for the unconstrained (integrable) motion are $(E, t), (a, \varepsilon)$ so that the motion leaves invariant the volume $dEdtda d\varepsilon$ and this implies that $da d\varepsilon$ is invariant under the map.*

[59] *Actually the problem of the ergodicity of the map $(a, e) \to (a', e')$ in systems integrable by quadratures (hence quasi periodic) in presence of reflections like the ones considered by Boltzmann might even be, as far as I know, an open problem, even in the case $\beta = 0$, i.e. in the Kepler problem case or in the similar harmonic potential case. And it might be that the confined motions of this system (integrable in absence of the obstacle) are even periodic for open regions of initial data at least if, in absence of obstacles, the system has only periodic motions: the stress on $\beta \neq 0$ suggests that Boltzmann might have thought so.*

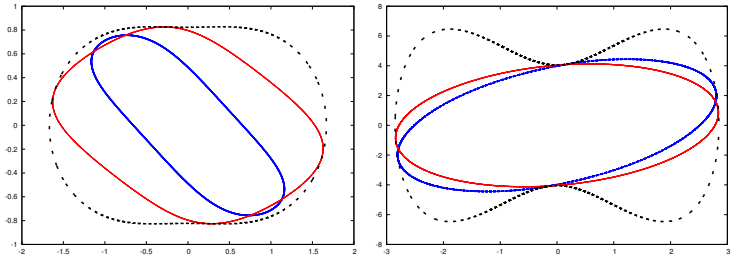

fig.4

Fig.4: Evolution of (x, a), with x abscissa of the collision point, different from (e, a) chosen by Boltzmann in his example but equivalent for the purpose of the density problem and, perhaps, simpler. Two orbits (drawn by points, although they look continuous) are enclosed in each domain of given energy (delimited by the external dotted loop). Uniqueness is not violated by the intersecting orbits as, at constant energy, the map to (x, a) variables is not $1 \longleftrightarrow 1$.

In each of Fig.4 two initial data with same energy move subject to a central force sum of a Newtonian attraction (left figure) or of a harmonic potential (right figure) and, furthermore, are elastically reflected upon collision with a straight line: the simulation appears to indicate (after 6.10^3 *iterations) that the motion is not dense on the energy surface.*
Simulations for the interaction considered by Boltzmann as well as the cases of purely harmonic or purely Newtonian potential (still with the straight line obstacle), lead to similar results at least for wide energy ranges. Density of the trajectories on energy surfaces can be expected in the above cases when the obstacle is "rougher" than a straight line, possibly already with an obstacle of equation $1 + \varepsilon \sin x$ *with* ε *large. For small* ε *there could be chaotic islands trapped between quasi periodic orbits and for large* ε *motion might be fully chaotic.*[60]
Heuristic analysis of the simulations results: from the first of the above figures it appears that there are data which seem to run on a quasi periodic orbit that remains well within the energy surface: and (via simulations) this remains true for data in a close enough region. Analysis of various cases seems to suggest that a purely gravitational potential ($\beta = 0$) *or a purely harmonic potential remain integrable and quasi periodic even in spite of collisions with the barrier. It has been pointed out*[61] *that if* $\beta > 0$ *is large the motions are chaotic on the energy surface.*

[60] *Data for figure on the right are:* $H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{b}{2}(x^2 + y^2) - \frac{g}{\sqrt{(x^2+y^2)}}$, *simulated with error of 5-th order, at step* $h = 10^{-3}$, *with* $b = 2., g = 0.1$, $x = 2.8, y = 1$ *and* $u = .3, v = .7$ *or* $u \longleftrightarrow v$, $H = E = 9.096366$. *In figure on the left* $H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{b}{2(x^2+y^2)} - \frac{g}{\sqrt{(x^2+y^2)}}$, *with* $b = .4, g = 1.$,$x = 1.0824, u = .15189, v = .477131, y = 1.$ *or* $u \longleftrightarrow v$, $H = E = -.5302125$. *It suggests that, in the considered models, the energy surface is not in general covered densely by a single trajectory.*

[61] I am indebted to I. Jauslin for informing me of the results of simulations that he performs to test existence of chaotic motions for large β, hence non-integrability in general for $\beta \neq 0$.

Then for β small, if the potential is augmented by a centrifugal barrier ($\beta > 0$) and, at least within a region in which motions do not touch the boundary of the constant energy domain, the map $(x, a) \to (x', a')$ remains smooth and generates quasi periodic motions on smooth curves: this would be consistent because introduction of the extra centrifugal barrier could be considered a perturbation and the KAM theorem, Moser [1962], might be applicable and guarantee that large portions of the energy surface are covered by quasi periodic motions, developing on smooth curves with possible chaotic motions between them. Deformation of the obstacle into $y = 1 + \varepsilon \sin(x)$ is also a perturbation to which KAM theorem should be applicable (if all motions are periodic in absence of any added centrifugal barrier ($\beta = 0$)). Hence, for ε small, we could expect coexistence of chaotic motions trapped between near pairs of motions on closed orbits run quasi periodically (KAM) and delocalization or, at least, large chaotic regions can be expected at large β (and observed) or large ε; could full delocalization (i.e. density of motion of almost all initial data) in the energy surface be expected?

It should also be remarked that the cases in which the obstacle line passes through the attraction point (i.e. $\gamma = 0$) are maifestly integrable, even in presence of the centrifugal force: and a relation with KAM theory could also be attempted by considering γ as a perturbation parameter.

E Equilibrium inside molecules (Trilogy: #1)

Quotes and comments on: *Über das Wärmegleichgewicht zwischen mehratomigen Gasmolekülen*, 1871, [Boltzmann, 1871b, #18,p.237-258].

[*This work complements the last section of [Boltzmann, 1868a, #5] in the sense that it can be seen as a different viewpoint towards an application of the general result contained in it. It is remarkable particularly for its Sec.II where Maxwell's distribution is derived as a consequence of the of the assumption that, because of the collisions with other molecules, the atoms of the molecule visit all points of the phase space of the molecule. It is concluded that the distribution of the atoms inside a molecule is, in the center of mass frame, a function of the center of mass average kinetic energy, i.e. of the temperature $\frac{1}{h}$, and of the total energy in the center of mass, sum of kinetic energy K, in the center of mass, and of the internal potential energy χ, proportionally to $e^{-h(K+\chi)}$.*
So the distribution of the coordinates of the body will depend on the total average energy (just kinetic as the distance between the particles is assumed to be very large compared with the interaction range). The form of the distribution is not obtained by supposing the particles energies discretized regularly, as done in [Boltzmann, 1868a, #5], but exploiting invariance properties. The question of uniqueness of the canonical distribution is explicitly raised, [Boltzmann, 1871b, #18,p.255]: the determined distribution (i.e. the canonical distribution) might be not the unique invariant distribution: this shows that a doubt now entered Boltzmann's mind which had not arisen at the time of the works [Boltzmann,

1868a, #5] and [Boltzmann, 1868b, #6] (see above), where an invariant distribution was found but its possible uniqueness was not brought up, see Appendix C. The invariance arguments used leave open the doubt about uniqueness. The relation of the "Trilogy" papers with Einstein's statistical mechanics is discussed in [Renn, 1997].]

According to the mechanical theory of heat every molecule of gas while in motion does not experience, by far for most of the time, any collision; and its baricenter proceeds with uniform rectilinear motion through space. When two molecules get very close, they interact via certain forces, so that the motion of each feels the influence of the other.

The different molecules of the gas take over all possible configurations [62] and it is clear that it is of the utmost importance to know the probability of the different states of motion.

We want to compute the average kinetic energy, the average potential energy, the mean free path of a molecule &tc. and, furthermore, also the probability of each of their values. Since the latter value is not known we can then at most conjecture the most probable value of each quantity, as we cannot even think of the exact value.

If every molecule is a point mass, Maxwell provides the value of the probability of the different states (Phil. Mag., March[63] 1868), [Maxwell, 1866]. In this case the state of a molecule is entirely determined as soon as the size and direction of its velocity are known. And certainly every direction in space of the velocity is equally probable, so that it only remains to determine the probability of the different components of the velocity.

If we denote N the number of molecules per unit volume, Maxwell finds that the number of molecules per unit volume and speed between c and $c + dc$, equals, [Maxwell, 1866, Eq.(26),p.187]:

$$4\sqrt{\frac{h^3}{\pi}} N e^{-hc^2} c^2 \, dc,$$

where h is a constant depending on the temperature. We want to make use of this expression: through it the velocity distribution is defined, *i.e.* it is given

[62] *In this paper Boltzmann imagines that a molecule of gas, in due time, goes through all possible states: this is not yet the ergodic hypothesis because this is attributed to the occasional interaction of the molecule with the others. The hypothesis is used to extend the hypothesis formulated by Maxwell for the monoatomic systems to the case of polyatomic molecules. For these he finds the role of the internal potential energy of the molecule, which must appear together with the kinetic energy of its atoms in the stationary distribution. The results agree with the earlier work [Boltzmann, 1868a, #5] where, without even assuming very low density, the microcanonical distribution for the entire system was found by supposing that the equilibrium state distribution had a unique positive density on the available phase space and was determined by a combinatorial count of the possible configurations. Here no combinatorial count is done and only uniqueness of a distribution with positive density is used together with negligibility of multiple collisions: the latter assumption however, as it is stressed, casts doubts on the uniqueness of the distribution.*

[63] *Maybe February?*

how many molecules have a speed between 0 and dc, how many between dc and $2dc$, $2dc$ and $3dc$, $3dc$ and $4dc$, etc. up to infinity.

Natural molecules, however, are by no means point masses. We shall get closer to reality if we shall think of them as systems of more point masses (the so called atoms), kept together by some force. Hence the state of a molecule at a given instant can no longer be described by a single variable but it will require several variables. To define the state of a molecule at a given instant, think of having fixed in space, once and for all, three orthogonal axes. Trace then through the point occupied by the baricenter three orthogonal axes parallel to the three fixed directions and denote the coordinates of the point masses of our molecule, on every axis and at time t, with $\xi_1, \eta_1, \zeta_1, \xi_2, \eta_2, \zeta_2, \ldots, \xi_{r-1}, \eta_{r-1}, \zeta_{r-1}$. The number of point masses of the molecule, that we shall always call atoms, be r. The coordinate of the r-th atom be determined besides those of the first $r-1$ atoms from the coordinates of the baricenter. Furthermore let c_1 be the velocity of the atom 1, u_1, v_1, w_1 be its components along the axes; the same quantities be defined for the atom 2, c_2, u_2, v_2, w_2; for the atom 3 let them be c_3, u_3, v_3, w_3 &tc. Then the state of our molecule at time t is given when the values of the $6r-3$ quantities $\xi_1, \eta_1, \zeta_1, \xi_2, \ldots, \zeta_{r-1}, u_1, v_1, w_1, u_2, \ldots, w_r$ are known at this time. The coordinates of the baricenter of our molecule with respect to the fixed axes do not determine its state but only its position.

We shall say right away, briefly, that a molecule is at a given place when its baricenter is there, and we suppose that in the whole gas there is an average number N of molecules per unit volume. Of such N molecules at a given instant t a much smaller number dN will be so distributed that, at the same time, the coordinates of the atom 1 are between ξ_1 and $\xi_1 + d\xi_1$, η_1 and $\eta_1 + d\eta_1$, ζ_1 and $\zeta_1 + d\zeta_1$, those of the atom 2 are between ξ_2 and $\xi_2 + d\xi_2$, η_2 and $\eta_2 + d\eta_2$, ζ_2 and $\zeta_2 + d\zeta_2$, and those of the $r-1$-th between ξ_{r-1} and $\xi_{r-1} + d\xi_{r-1}$, η_{r-1} and $\eta_{r-1} + d\eta_{r-1}$, ζ_{r-1} and $\zeta_{r-1} + d\zeta_{r-1}$, while the velocity components of the atom 1 are between u_1 and $u_1 + du_1$, v_1 and $v_1 + dv_1$, w_1 and $w_1 + dw_1$, those of the atom 2 are between u_2 and $u_2 + du_2$, v_2 and $v_2 + dv_2$, w_2 and $w_2 + dw_2$, and those of the $r-1$-th are between u_{r-1} and $u_{r-1} + du_{r-1}$, v_{r-1} and $v_{r-1} + dv_{r-1}$, w_{r-1} and $w_{r-1} + dw_{r-1}$.

I shall briefly say that the so specified molecules are in the domain (A). Then it immediately follows[64] that

$$dN = f(\xi_1, \eta_1, \zeta_1, \ldots, \zeta_{r-1}, u_1, v_1, \ldots, w_r) d\xi_1 d\eta_1 d\zeta_1 \ldots d\zeta_{r-1} du_1 dv_1 \ldots dw_r.$$

I shall say that the function f determines a distribution of the states of motion of the molecules at time t. The probability of the different states of the molecules would be known if we knew which values has this function for each considered gas when it is left unperturbed for a long enough time, at constant density and temperature. For monoatomic molecules gases Maxwell finds that the function f has the value

$$4\sqrt{\frac{h^3}{\pi}} N e^{-hc^2} c^2 \, dc.$$

[64] *Here it is assumed the the equilibrium distribution has a density on phase space.*

The determination of this function for polyatomic molecules gases seems very difficult, because already for a three atoms complex it is not possible to integrate the equations of motion. Nevertheless we shall see that just from the equations of motion, without their integration, a value for the function f is found which, in spite of the motion of the molecule, will not change in the course of a long time and therefore, represents, at least, a possible distribution of the states of the molecules.[65]

That the value pertaining to the function f could be determined without solving the equations of motion is not so surprising as at first sight seems. Because the great regularity shown by the thermal phenomena induces to suppose that f be almost general and that it should be independent from the properties of the special nature of every gas; and also that the general properties depend only weakly from the general form of the equations of motion, except when their complete integration presents difficulties not unsurmountable.[66]

Suppose that at the initial instant the state of motion of the molecules is entirely arbitrary, *i.e.* think that the function f has a given value.[67] As time elapses the state of each molecule, because of the motion of its atoms while it follows its rectilinear motion and also because of its collisions with other molecules, becomes steady; hence the form of the function f will in general change, until it assumes a value that in spite of the motion of the atoms and of the collisions between the molecules will no longer change.

When this will have happened we shall say that the states of the molecules are distributed in *thermal equilibrium*. From this immediately the problem is posed to find for the function f a value that will not any more change no matter which collisions take place. For this purpose we shall suppose, to treat the most general case, that we deal with a mixture of gases. Let one of the kinds of gas (the kind G) have N molecules per unit volume. Suppose that at a given instant t there are dN molecules whose state is in the domain (a). Then as before

$$dN = f(\xi_1, \eta_1, \zeta_1, \ldots, \zeta_{r-1}, u_1, v_1, \ldots, w_r) d\xi_1 d\eta_1 d\zeta_1 \ldots d\zeta_{r-1} du_1 dv_1 \ldots dw_r. \tag{1}$$

The function f gives us the complete distribution of the states of the molecules of the gas of kind G at the instant t. Imagine that a certain time δt elapses. At time $t + \delta t$ the distribution of the states will in general have become another, hence the function f becomes different, which I denote f_1, so that at time $t + \delta t$ the number of molecules per unit volume whose state in the domain (A) equals:

$$f_1(\xi_1, \eta_1, \ldots, w_r)\, d\xi_1\, dh_1\, \ldots\, dw_r. \tag{2}$$

§I. Motion of the atoms of a molecule

[65] *Remark the care with which the possibility is not excluded of the existence invariant distributions different from the one that will be determined here.*

[66] *Boltzmann is aware that special behavior could show up in integrable cases: he was very likely aware of the theory of Lagrange's solution of the harmonic chain, [Lagrange, 1867-1892, Vol.I].*

[67] *This is the function called "empirical distribution", [Goldstein and Lebowitz, 2004, Garrido et al., 2005].*

[(p.241):*Follows the analysis of the form of f if the collisions can be regarded as instantaneous compared to the average free flight time: Liouville's theorem, for pair collisions, is derived from scratch and it is shown that if f is invariant then it has to be a function of the coordinates of the molecules through the integrals of motion. This is a wide extension of the argument for monoatomic gases in [Maxwell, 1866].*]

§II. Collisions between molecules

[(p.245):*It is shown that to have a stationary distribution also in presence of binary collisions it suffices (p.254,l.6) that the function f has the form $Ae^{-h\varphi}$ where φ is the total energy, sum of the kinetic energy and of the potential energy of the atoms of the molecule, in the center of mass. Furthermore if the gas consists of two species then h must be the same constant for the distribution of either kinds of molecules and it is identified with the inverse temperature.*
Since a gas, monoatomic or not, can be considered as a giant molecule it is seen that this is also a derivation of the microcanonical distribution if no other constants of motion besides the total energy (implicit in the last section of the [Boltzmann, 1868a, #5] work, see comments at the end of AppendixC) is assumed for the entire gas.
The kinetic energies equipartition and the ratios of the specific heats is deduced. It becomes necessary to check that this distribution "of thermal equilibrium" generates average values for observables compatible with the heat theorem: but this will be done in the successive paper of the trilogy, [Boltzmann, 1871d, #20]. There it will also be checked that the hypothesis that each group of atoms that is part of a molecule passes through all states compatible with the value of the energy (possibly with the help of the collisions with other molecules) leads to the same result if the number of molecules is infinite (with finite density) or very large (in a container).
It is instructive that Maxwell comments (somewhat unfairly?) the assumptions of short duration of the collisions and the lack of multiple collisions as "It is true that in following the steps of the investigation, as given either by Boltzmann or by Watson, it is difficult, if not impossible, to see where the stipulation about the shortness and the isolation of the encounters is made use of. We may almost say that it is introduced rather for the sake of enabling the reader to form a more definite mental image of the material system than as a condition of the demonstration.", *[Maxwell, 1879, p.714,l.2].*
The uniqueness of the equilibrium distribution of the atoms in a molecule rests on the nonexistence, for isolated molecules, of other constants of motion besides the energy and the question is left open as explicitly stated at p.255, see below: the problem arises because the argument is based on the conservation law in pair collisions and here Boltzmann acknowledges that there might be problems in presence of multiple collisions (actually there is a problem even in absence of other constants of motion for isolated molecules); nevertheless he points out that the distribution found is a possible stationary distribution:]

p.255, (l.21) Against me is the fact that, until now, the proof that these distributions are the only ones that do not change in presence of collisions is not complete. Nevertheless remains the fact that [the distribution shows] that the same gas with equal temperature and density can be in many states, depending on the given initial conditions, *a priori* improbable and which will even never be observed in experiments.

[*The uniqueness problem suggests the idea, see the next AppendixF, of considering n copies of the entire system (of molecules or atoms in a gas) not interacting at all and apply again the argument of this paper (that the distribution of the states has to be a (positive, being a frequency of visit) function in the region compatible with the assigned values of the constants of motion): in absence of other constants of motion, beyond the total energy, it will follow that the equilibrium distribution must be the microcanonical one which will also imply a canonical distribution for the single molecules: this will be the subject of the immediately following work, [Boltzmann, 1871c, #19], which can be considered the first in which an "ensemble" in the modern sense appears, [Gibbs, 1902, Inaba, 2015]. It is worth reporting a comment in [Maxwell, 1879, p.715], on this matter: "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".*
This paper is also important as it shows that Boltzmann was well aware of the paper [Maxwell, 1866]: in which key steps towards the Boltzmann's equation is discussed in great detail. One can say that Maxwell's analysis yields a form of "weak Boltzmann's equation", namely several equations which can be seen as equivalent to the time evolution of averages of one particle observable with what we call now the one particle distribution of the particles. Boltzmann will realize that the one particle distribution itself obeys an equation (Boltzmann's equation) and will obtain in this way a major conceptual simplification of Maxwell's approach and derive the H-theorem, [Boltzmann, 1872, #22].]

F Microcanonical ensemble and ergodic hypothesis (Trilogy: #2)

Quotes and comments on: *Einige allgemeine Sätze über Wärmegleichgewicht*, (1871), [Boltzmann, 1871c, #19].

§I. *Correspondence between the theorems on the polyatomic molecules behavior and Jacobi's principle of the last multiplier.* [68]

[68] *This title is quoted by Gibbs in the introduction to his Elementary principles in statistical mechanics, [Gibbs, 1902], thus generating some confusion because this title is not found* in the list of publications by Boltzmann.

The first theorem that I found in my preceding paper *Über das Wärmegleichgewicht zwischen mehratomigen Gasmolekülen*, 1871, [Boltzmann, 1871b, #18] (see also AppendixE above),[69] is strictly related to a theorem, that at first sight has nothing to do with the theory of gases, *i.e.* with Jacobi's principle of the last multiplier.

To expose the relation, we shall leave aside the special form that the mentioned equations of the theory of heat have, whose relevant developments will be generalized here later.

Consider a large number of systems of point masses (as in a gas containing a large number of molecules of which each is a system of point masses). The state of a given system of such points at a given time is assigned by n variables $s_1, s_2, \ldots, s_n$ for which we can pose the following differential equations:

$$\frac{ds_1}{dt} = S_1, \frac{ds_2}{dt} = S_2, \ldots, \frac{ds_n}{dt} = S_n.$$

Let $S_1, S_2, \ldots, S_n$ be functions of $s_1, s_2, \ldots, s_n$ and possibly of time. Through these equations and the initial value of the n variables $s_1, s_2, \ldots, s_n$ are obtained the values of such quantities at any given time. To arrive to the principle of the last multipliers, we can use many of the conclusions reached in the already quoted paper; hence we must suppose that between the point masses of the different systems of points never any interaction occurs. As in the theory of gases the collisions between molecules are neglected, also in the present research the interactions will be excluded.

[*In the present paper the purpose it to replace the assumption on the absence of*

[69] *It might be useful to summarize the logic behind this reference.*
In the quoted paper, [Boltzmann, 1868a, #5], a gas of n molecules was supposed to be at so low density that the duration of the collisions could be negelected: so kinetic energy would be conserved and molecules, as systems of atoms, would evolve independently for all but a neglegible fraction of time. If the position of the baricenter of each molecule was not considered, the state of the system could be seen as a collection of molecules of r atoms each, evolving in time independently.
Each molecule would be in a state represented by a point in a $6r-3$ dimensional phase space and a state of the gas would be a point in a $(6r-3)n$ dimensional phase space. At collisions, assuming that multiple collisions could be neglected, the states of the colliding pairs would vary: but, in a stationary state of the gas, the changes due to collisions would not cause a change in the average number of molecules with a given state.
The latter has to be identified with the fraction of time each molecule spends in the state. Hence one has only to look at the whole region in the $(6r-3)n$-dimensional phase space, in which can be found the point representing the state, in order to find the (hopefully unique) probability density invariant under the collisions dynamics (between pairs of molecules).
A first problem then is to find the phase space region that will be visited by the system: it will be determined "under an hypothesis", namely that this will be the $(6r-3)n-1$ dimensional region in which the total kinetic energy (denoted $n\kappa$) has a given value, and a second problem is to find the density (which Boltzmann implicitly assumes to be smooth) representing the count of molecules near a phase space point. The second problem was solved easily if multiple collisions and pairs collisions duration were negligible: there is only one possibility (as it is reluctantly admitted, see [Boltzmann, 1871b, #18,p.251] and comments to the Appendix E above)for the density, namely it has to be a function of the total kinetic energy, as he shows (with an argument going back to Maxwell). It follows that the density is constant on the surface and all it remained to do was to evaluate the probability of events of interest.

multiple collisions with an hypothesis that, in an equilibrium state, all configurations compatible with the given value of the total energy must be visited by the phase space point representing the state of the system. The new hypothesis is the ergodic hypothesis.
As an application the microcanonical distribution for the total rarefied gas and, as its consequence, the canonical distribution of the states of the single molecules are derived.

This paper is not only important because it goes beyond the low density assumption in the general case and the no multiple collisions assumptions in the case of rarefied gas of molecules. Boltzmann imagines the general system as a giant molecule and, following the idea applied to the molecules of a gas, the statistics is given by considering a large number of copies of the system without reciprocal interaction (as the molecules in a rarefied gas of [Boltzmann, 1871b, #18]) and supposing that the entire phase space is the set of given total energy $n\kappa$ (kinetic) (plus potential) is visited by their independent motions. This is the hypothesis that no other constants of motion beyond the conservation laws exist[70] *and that the phase point representing the state visits all neighborhoods of the phase space. At the same time it is the first appearance, as noted in [Gibbs, 1902], of what is often called an "ensemble": for a thorough discussion of the notion and use of the ensembles see the recent analysis in [Inaba, 2015]. Conceiving the state of a system as described by the density of frequency of visit to regions of phase space or by the number of identical non interacting copies of the system that fall in the regions is equivalent if the density of frequency or if, respectively, the number of copies falling in the regions, are invariant under the time evolution: the first view is mostly used by Boltzmann, except in this work, and the second is preferred by Maxwell in his last work on statistical mechanics, [Maxwell, 1879].*

The case in which there is only one constant of motion was already solved in the earlier work. Furthermore in this paper the case of several constants of motion is also considered. Actually most of the paper is dedicated to the computation of the Jacobian determinant necessary to compute the surface element of the surface defined by the values of the constants of motion. The calculation is based on the Lecture 12, about the "principle of the last multiplier", in Jacobi's Lectures on Mechanics, [Jacobi, 1884], see also [Whittaker, 1917 (reprinted 1989, p.277],[71] *which Boltzmann rederives here, presenting it from scratch (in 24 pages!). Extensions of Liouville's theorem are discussed and used to express the form of the distribution at fixed values of of $n - k$ constants of*

[70] *It has to be kept in mind that Boltzmann usually only considers smooth functions (e.g., if functions of time, twice differentiable, see his axiom 2 of Mechanics, [Boltzmann, 1897, p.10]).*

[71] *Lagrange's multipliers method of enforcing holonomic constraints consists in adding extra forces suitably determined to impose the constraints. In Jacobi's lectures, assuming that in a n-dimensional ODE $n - 1$ constants of motion are known, a last one, the last constant of motion, can be found (and its construction is reducible to a quadrature of an exact differential) and can be associated with the "missing" or "last" Lagrange multiplier. The method involves a long analysis of various Jacobian determinants which are used by Boltzmann to evaluate the Jacobian determinants needed in his work in cases in which the number of constants of motion is* 1 *(total energy) or at most* 7 *(energy, momentum and angular momentum).*

motion; concluding that the distribution is deduced by dividing by the appropriate Jacobian determinant of the transformation expressing k free coordinates in terms of the $n-k$ constants of motion: the last multiplier of Jacobi is just the Jacobian determinant of the change of coordinates.

§II. *Thermal equilibrium for a finite number of point masses.*

[(p.269)*In this section the method of §I is applied to compute the average kinetic energy and the average potential energy in a system with n point particles and $n-k$ constants of motion $\varphi_n, \dots, \varphi_{k+1}$. The arguments of Sec. I,II in modern language would be the following. It is assumed, with no discussion, that the motion visits the entire region where φ_j have given values and which is connected to the initial values of interest (usually this region is connected), (p.271,l.15). It is also assumed that there are no further constants of motion (keeping in mind that Boltzmann never really considers non smooth functions, except occasionally when dealing with hard core collisions). Then, if a distribution defined on the whole phase space is stationary, it must have the form $f(\varphi_n, \varphi_{n-1}, \dots, \varphi_{k+1}) ds_1 ds_2 \dots ds_n$: but we are interested on the distribution with given values $a_n, \dots, a_{k+1}$ of the constants of motion. Hence we would say that it has the form*

$$f(\varphi_n, \varphi_{n-1}, \dots, \varphi_{k+1}) \, (\prod_{j=k+1}^{n} \delta(\varphi_j - a_k)) ds_1 ds_2 \dots ds_n$$

Therefore the probability distribution density for $s_1, \dots, s_k$ is

$$\int f(\varphi_n, \varphi_{n-1}, \dots, \varphi_{k+1}) \, (\prod_{j=k+1}^{n} \delta(\varphi_j - a_k)) ds_{k+1} ds_{k+2} \dots ds_n$$

where the integral is over the variables $s_n, \dots, s_{k+1}$; hence developing the delta functions it is

$$f(\varphi_n, \varphi_{n-1}, \dots, \varphi_{k+1}) \, \frac{1}{\frac{\partial(\varphi_n, \dots, \varphi_{k+1})}{\partial(s_n, \dots, s_{k+1})}} \Big|_{\varphi_n = a_n, \dots \varphi_{k+1} = a_{k+1}}$$

This formula is derived, in 24 pages, via use of the principle of the last multiplier and illustrated by a few examples on quasi periodic motions in simple 2 dimensional force fields, in which there are up to two constants of motion (energy and, possibly, angular momentum).
It is then applied, at the end of Sec.II, to the derivation of the microcanonical ensemble in the general case with $k = n-1$ (i.e. the energy being the only conserved quantity), already obtained in general by a combinatorial argument in [Boltzmann, 1868a, #5] and via the conservation laws in binary collisions and assuming instantaneous duration of collisions, see AppendixE, in [Boltzmann, 1871b, #18].
Here the two assumptions are replaced by positivity of the distribution density

on the surface defined by all the constants of motion: therefore it is an assumption implicit in [Boltzmann, 1868a, #5], as recognized in [Maxwell, 1879] and quoted above, but the method is very different from both the earlier derivations. Assuming non existence of other constants of motion is a form of the ergodic hypothesis if non smooth constants of motion are not allowed; a natural assumption, see [Boltzmann, 1897, p.10,V.1], whose importance has not been always realized: e.g. it led Fermi to think to have proved the generic ergodicity in mechanical systems, [Fermi, 1923a,b] (later he brilliantly corrected himself in [Fermi, 1965, Vol.2,p.977]).]

§III.(p.284) *Solution for the thermal equilibrium for the molecules of a gas with a finite number of point masses under an hypothesis.*

Finally from the equations derived we can, under an assumption which it does not seem to me of unlikely application to a warm body, directly access to the thermal equilibrium of a polyatomic molecule, and more generally of a given molecule interacting with a mass of gas. The great chaoticity of the thermal motion and the variability of the force that the body feels from the outside makes it probable that the atoms get in the motion, that we call heat, all possible positions and velocities compatible with the equation of the kinetic energy, and even that the atoms of a warm body can take all positions and velocities compatible with the last equation considered.

[*The hypothesis, used already in the context of general evolution equations at p.271,l.15, and in similar form earlier (see above), that is formulated here explicitly for systems of atoms is that the atoms of a "warm body" containing a molecule take all positions and velocities. This is the first time the ergodic hypothesis is formally stated almost in the form in which it is still intended today (the exceptions occurring on a set of zero volume in phase space are not mentioned: not because they are overlooked but, as discussed in Sec.7,8,9 above, because of the discrete view of phase space.):*
The logic of the paper seems to be the followimg. To compute the time averages consider the accessible phase space points, i.e. compatible with the constraints. Consider all points as independent systems placed in phase space with a density which has to be invariant under time evolution because the points will move and others occupy their places.
Boltzmann considers only distributions with a density and appears to think that the density has to be positive (being proportional to a frequency of visit). Of course if the system admits constants of motion $\varphi_n, \dots, \varphi_{k+1}$ the phase space is reduced to the surface, that I shall call Σ, defined by the constants of motion: therefore the density, which would be constant on the energy surface if the energy was the only constant of motion, on Σ is obtained in modern language by the distribution $\prod_{i=n}^{k+1} \delta(\varphi_i - a_i)$ times a function invariant on Σ, hence constant (by the hypothesis); the evaluation of the delta functions requires the computation of a Jacobian (the last multiplier).
The Jacobi's principle, in this paper, is the theorem that expresses the volume

element in a system of coordinates in terms of that in another through a "multiplier" (the "Jacobian determinant" of the change of coordinates). Boltzmann derived, already in the preceding paper, what we call today "Liouville's theorem" for the conservation of the volume element of phase space and here he gives a version that takes into account the existence of constants of motion, such as the energy.
At the same time this work lays the foundations of the theory of the statistical ensembles, as recognized by Gibbs in the introduction of his treatise on statistical mechanics, [Gibbs, 1902]: curiously Gibbs quotes this paper of Boltzmann attributing to it a title which, instead, is the title of its first Section, [Boltzmann, 1871e, see]. From the uniform distribution ("microcanonical") on the surface of constant total energy (suggested by the above interpretation of the ergodic hypothesis) the canonical distribution of subsystems (like molecules or atoms) follows by integration and use of the formula $(1 - \frac{c}{\lambda})^{\lambda} = e^{-c}$ *if* λ *(total number of molecules) is large.*
It appears that Boltzmann by making the "Hypothesis", that the atoms of a warm body can take all positions and velocities compatible with the equation of the kinetic energy, assumes that the only such distribution is the one which, as he shows, is constant on the energy surface, because of the Liouville's theorem that he derives in several others among his papers, and in particular in the first of the trilogy and of the idea that the distribution is positive in the regions visited by the phase space point. This has been mathematized as the "metric transitivity" form of ergodicity. The "doubt" that "perturbed" him in the first paper of the trilogy, see above, does not show up in this work (the reason is that he was certainly not thinking to the possible existence of non smooth constants of motion, see [Boltzmann, 1897, p.10,V.1]).
The above form of the ergodic hypothesis assumed for the whole gas, is used in this last Section to derive the canonical distribution for the velocity and position distributions both of a single molecule and of an arbitrary number of them ($\ll n$)*. It goes beyond the preceding paper deducing the microcanonical distribution, on the assumption of the ergodic hypothesis, and finding as a consequence the canonical stationary distribution of the atoms of each molecule or of an arbitrary number of them by integration on the positions and velocities of the other molecules.*
Hence, imagining the gas large, the canonical distribution follows for every finite part of it, be it constituted by 1 *or by* 10^{19} *molecules: a finite part of a gas is like a giant molecule.*]

Let us accept this hypothesis, and thus let us make use of the formulae to compute the equilibrium distribution between a gas in interaction with a body supposing that only r of the mentioned λ atoms of the body interact with the mass of gas.

Then χ [*potential energy*] has the form $\chi_1 + \chi_2$ where χ_1 is a function of the coordinates of the r atoms, χ_2 is a function of the coordinates of the remaining $\lambda - r$. [72]

[72] *Additivity of the potential reflects the assumption that density is low and intermolecular*

...

[*The derivation of the canonical distribution for the molecules from the microcanonical one for the whole gas, at small density to reproduce the results of [Boltzmann, 1871b, #18]: the derivation is the one still taught today.*]

... These equations must, under our hypothesis, hold for an arbitrary body in a mass of gas, and therefore also for a molecule of gas. In the considered case it is easy to see that this agrees with the formulae of my work *Über das Wärmegleichgewicht zwischen mehratomigen Gasmolekülen*, 1871, [Boltzmann, 1871b, #18]. We also arrive there in a much easier way to what found there. However the proof, in the present section, makes use of the hypothesis about the warm body, certainly acceptable but which had not yet been proved: thus I avoided it in the quoted paper achieving the proof in a way independent from that hypothesis.[73]

G Heat theorem without dynamics (Trilogy: #3)

Quotes and Comment on: *Analytischer Beweis des zweiten Hauptsatzes der mechanischen Wärmetheorie aus den Sätzen über das Gleichgewicht des lebendigen Kraft*, 1871, [Boltzmann, 1871d, #20,p.288-308].

Here dynamics enters only through the conservation laws and the hypothesis (see the first trilogy paper [Boltzmann, 1871b, #18,Sec.III]) that never a multiple collision takes place and collisions duration is negligible because of low density. Alternatively it could be based on the ergodic hypothesis of [Boltzmann, 1871c, #19]. It is used at the beginning to start from the results of the earlier works leading to the microcanonical distribution for the entire warm body and to the canonical distribution for the smaller subsystems, see also AppendicesE,F above.
Referring to [Boltzmann, 1871b, #18] for motivation and going back to the quasi static processes of his early work, [Boltzmann, 1866, #2], and assuming right away the canonical distribution, it is shown that it also follows that defining the heat dQ received by the body, in an infinitesimal step of the process, as the variation of the total average energy dE plus the work dW done by the system on the outside (variation of the time average of the potential energy due to a change of the values of the external parameters) it follows that $\frac{dQ}{T}$ is an exact differential if T is proportional to the average kinetic energy.
This is the first introduction of the notion of "thermodynamic analogy" or

interaction, important to reach a stationary state, can be neglected in studying the molecules distributions in equilibrium. Thus the potetnial energy is just the interaction energy of the atoms inside the molecules to which they belong.

[73] *He means that he had proved the invariance of the canonical distribution (which implies the equidistribution) without the present hypothesis. However even that was not completely satisfactory for him (and for us), as he had also stated in the quoted paper, since he had not been able to prove the uniqueness of the solution found there (that we know today to be not unique in general).*

"model of thermodynamics": an example is exhibited by the canonical distribution; the novelty with respect to the 1866 theory is that the probability distribution of the microscopic configurations is also determined explicitly and reference to periodicity is formally avoided. The periodic motion of the system is replaced by a stationary probability distribution in the phase space: the two notions coincide if the ergodic hypothesis of [Boltzmann, 1871c, #19] is accepted. [74]
It will be revisited in the paper of 1884, [Boltzmann, 1884, #73], with the general theory of statistical ensembles and of the states of thermodynamic equilibrium.
This work also preludes to the molecular chaos analysis in the paper, following this a little later, developing "Boltzmann's equation", [Boltzmann, 1872, #22]. The first seven pages, from p.288 to p.294 are translated and commented as they are useful to understand the main ideas and the difference with the earlier works. The rest of the work deals with the concept of thermodynamic analogy which will be taken up and further developed in later works, [Boltzmann, 1877a,b, 1884, 1877-84], see the Appendices below.

Let (K) be an arbitrary body, consistig of r mass points (Atoms). We shall denote the coordinates of its atoms $x_1, y_1, \ldots, z_r$ and the velocities $c_1, c_2, \ldots, c_r$ and their corresponding three components $u_1, v_1, w_1, u_2, \ldots, w_r$. Finally let χ be the potential energy, also a function of of $x_1, y_1, \ldots, z_r$, whose negative gradient with respect to the coordinates of an atom give the force acting in the direction of the coordinates. Let us leave unchanged for a very long time the other circumstances (temperature and the external forces) to which the body is subject, and the fraction of T in which the variables $x_1, y_1, \ldots, z_r, u_1, v_1, \ldots, w_r$ are in the region

$$(A) \qquad x_1 \text{ and } x_1 + dx_1,\ y_1 \text{ and } y_1 + dy_1, \ldots,\ w_r \text{ and } w_r + dw_r$$

will be denoted τ. I denote the value τ/T as the time, during which *in average* the state of the body is enclosed in the region (A). I found in the quoted work, [75]aware of an underlying hypothesis and if the body is in contact with infinitely many molecules of a gas, that this ratio has the value

$$dt = \frac{e^{-h\varphi} dx_1 dy_1 dz_r, du_1 dv_1 \ldots dw_r}{\int\int \ldots e^{-h\varphi} dx_1 dy_1 dz_r, du_1 dv_1 \ldots dw_r} \tag{1}$$

[74] *In the 1866 work Boltzmann determined mechanical quantities analogus to temperature, specific heat, free energy directly from the definitions of the latter in rarefied gases kinetic theory, while entropy was obtained through the new idea that atoms follow periodic trajetories: distribution of the phase space points is even mentioned.*

[75] See note p.237 of Wissenshaeftliche Abhandlungen [*This footnote is added to the WA: however it points at [Boltzmann, 1871b, #18]: but it seems that it should point instead at [Boltzmann, 1871c, #19]]. The remark here is that the main object in this paper, i.e. the canonical distribution of the molecules, can be obtained via the work [Boltzmann, 1871c, #19] with its ergodic hypothesis or via [Boltzmann, 1871b, #18] with the low density, no multiple collisions assumptions.*

where

$$\varphi = \chi + \sum \frac{mc^2}{2}$$

This formula appears as the last formula of the quoted work[76] and there also is expressed the same probability of all the velocity components and is determined the suitable constant λ''.[77]

We know this expression, even without the deliberate key hypothesis, from my work [Boltzmann, 1871b, #18]. Let one molecule, among the ones of which the body is composed, contain ρ atoms. Let the coordinates of the baricenter of this molecule be x, y, z, let the coordinates if its atoms with respect to coordinate axes through the baricenter be $\xi_1, \eta_1, \ldots, \zeta_\rho$ and the velocities of the atoms parallel to the same axes be $\alpha_1, \beta_1, \ldots, \gamma_\rho$. The total kinetic energy contained in the molecule will be denoted φ^*.[78] Finally let the gas contain N molecules per unit volume. I find in the work [Boltzmann, 1871b, #18] that the number of those molecules of this gas per unit volume, for which at the same time $\xi_1, \eta_1, \ldots, \zeta_\rho, \alpha_1, \beta_1, \ldots, \gamma_\rho$ are in the region

$$(B) \qquad \xi_1 \text{ and } \xi_1 + d\xi_1,\ \eta_1 \text{ and } \eta_1 + d\eta_1, \ldots,\ \gamma_\rho \text{ and } \gamma_\rho + d\gamma_\rho$$

equals

$$dN = a\, e^{-h\varphi^*}\, d\xi_1 d\eta_1 \ldots d\gamma_\rho$$

where a and h are constants. The beginning of a collision of one of these molecules with the body (K), or of a collision between themselves, should again be characterized by a suitable function, of the relative position of the atoms of the body and of those of the colliding molecule, $F(x_1, y_1, \ldots, z_r, x, y, z, \xi_1, \eta_1, \ldots, \zeta_{\rho-1})$, indicating the beginning of a collision when it assumes a certain value b.[79]Re-acquisition of this value should mark the end of the collision. We shall denote temporarily the not yet known time τ within which, during a very long time T, the state of the body (K) is within the region (A), by $T \cdot g\, dx_1 dy_1 \ldots dw_r$, so that $g\, dx_1 dy_1 \ldots dw_r$ is also the [fraction of] time during which the state of the body is within the region (A).[80] Hence g is a function of the state of the body at the moment of the collision via $x_1, y_1, \ldots, z_r, u_1, v_1, \ldots, w_r$. The total state at the beginning of the collision is completely determined if we know the values of the $6r + 6\rho - 1$ quantities $x_1, y_1, \ldots, z_r, \xi_1, \eta_1, \ldots, \zeta_{\rho-1}, \alpha_1, \beta_1, \ldots, \gamma_\rho, x, y$ at this instant; z is determined

[76] *[Boltzmann, 1871c, #19,p.287]*

[77] *Should be C''.*

[78] *For consistency with the last formula φ^* should be the total energy in the center of mass, not just the kinetic energy. Also here it is somewhat confusing that from now on the body (K) will not contain the selected molecule although up to this point the molecule was part of (K).*

[79] *Remark that F does not depend on velocities.*

[80] *This anticipates the assumption, that will be made shortly, that the collisions duration can be neglected together with the time interval between collisions of some molecule of the body (K) and the extra molecule, as well as collisions between the molecule and more than just one molecule of (K).*

at the collision beginning by the equality $F = b$.[81] By an analysis closely similar to the one I have employed in the work [Boltzmann, 1871b, #18], it follows that the number of collisions that take place during the time T and in which, at the moment of their beginning, the atoms are in the region

$$(C) \qquad \begin{cases} \text{variables of the body (K)} \ \in \ (A) \\ \text{variables of the molecule} \ \in \ (B) \\ \text{at the same time } x \in (x, x+dx), \ y \in (y, y+dy), \end{cases}$$

is equal to

$$dm = \tau \, dN \, \omega dx dy = Tgae^{-h\varphi^*} \omega dx_1 dy_1 \dots dw_r d\xi_1 d\eta_1 \dots d\gamma_\rho dx dy \qquad (2)$$

where[82]

$$\omega = \frac{1}{\frac{\partial F}{\partial z}} \Big(\frac{\partial F}{\partial x_1} \frac{dx_1}{dt} + \frac{\partial F}{\partial y_1} \frac{dy_1}{dt} + \dots + \frac{\partial F}{\partial z} \frac{dz}{dt} \Big)$$

The variables determining the state of the interacting body, when at the beginning of the collision are in the region (C), shall be in the region

$$(D) \qquad \begin{cases} X_1 \text{ and } X_1 + dX_1, \ Y_1 \text{ and } Y_1 + dY_1, \dots W_r \text{and } W_r + dW_r \\ \Xi_1 \text{ and } \Xi_1 + d\Xi_1, \ H_1 \text{ and } H_1 + dH_1, \dots Y \text{and } Y + dY \end{cases}$$

Then, as in my quoted work, also follows the equation

$$\omega \cdot D = \Omega \qquad (3)$$

where D is the determinant

$$\sum \pm \frac{\partial x_1}{\partial X_1} . \frac{\partial y_1}{\partial Y_1} \cdots \frac{\partial w_r}{\partial W_r} . \frac{\partial \xi_1}{\partial \Xi_1} . \frac{\partial \eta_1}{\partial H_1} \cdots \frac{\partial y}{\partial Y}$$

With Ω, G, Φ^* we shall denote the quantities into which ω, g, φ are changed, if the $X_1, Y_1, \dots$ replace $x_1, y_1, \dots$. The number of collisions, taking place in the time T, in which the variables lie at the beginning in the region (D) is [83]

$$dM = TGae^{-h\Phi^*} dX_1 dY_1 \dots dW_r d\Xi_1 \dots dY \qquad (4)$$

We can thus express $X_1, Y_1, \dots$ as functions of $x_1, y_1, \dots$ or viceversa $x_1, y_1, \dots$ as functions of $X_1, Y_1, \dots$. So does the last terms in the formula (2) become

$$dm = Tgae^{-h\varphi^*} \omega D dX_1 dY_1 \dots dW_r d\Xi_1 \dots dY \qquad (5)$$

[81] *These are coordinates for the state of (K) and of the molecule, not just of the state of (K).*

[82] *The sign of ω is not taken into account. This is similar to arguments familiar in the context of the Boltzmann equation: $dN \, \dot{F} \, \delta(F - b)$ is the number of collisions per unit time and $\int dN \, \dot{F} \, \delta(F-b)dt$. The dN is $e^{-h\varphi^*} dx_1 \dots dw_r d\xi_1 \dots \zeta_{\rho-1} dxdydz$ and the formula follows by eliminating z via the delta function and integrating over t (obtaining τ).*

[83] *In Eq. (4) it seems that a should be instead A.*

This is the number of collisions which, during the time T take place and at their end have the variables in the region (D). It is possible to think also g, ω and φ^* as expressed as functions of $X_1, Y_1, \ldots$. Let us integrate dm over all possible variables of the state of the molekule $\Xi_1, H_1, \ldots, Z_{\rho-1}, X, Y$, thus we obtain the number of all collisions which during the time T take place so that at their end the state of the body its variables are in the region

$$(E) \qquad X_1 \text{ and } X_1 + dX_1,\ Y_1 \text{ and } Y_1 + dY_1, \ldots W_r \text{ and } W_r + dW_r$$

while the state of the molecule are not subject to any restriction. This number will be denoted $\int dm$ (where the integration is extended to the state variables for the molecule). We now wish to make a special assumption, although not realized in nature, but dealing with a conceivable case which will facilitate the calculation in the general cases. Namely we wish to assume that the collisions happen so frequently that immediately if a collision terminates again the next begins, while the body never experiences collisions involving two molecules, so that if the variables determining the state of the body are in the region (E) at the end of a collision again in a new collision in no way (or neglegibly) the movement of the atoms without collisions escapes this region. Hence, while the body is involved in a collision with a molecule no second collision occurs, so that we want to exclude from the time T these times and understand them as not included in T the totality of all instants in which no molecule endures a collision. Under this assumption the number of collisions, which so take place, in which at their end the variables are in the region (E) have to be equal to the number which at the [collision] beginning are in (E). Then first is the frequency in which the variables are entering these regions and secondly also the frequency of exiting, as, according to our assumption, the number of entrances and exits as a result of the movement of the atoms without collisions with the molecule can be neglected. The first number is $\int dm$, the second gives the expression of the integral of equation (4) over all values determining the state of the molecule. It will be denoted $\int dM$. It is also clear that this is the only condition on the determination of the function g. But the condition $\int dm = \int dM$ is satisfied, if

$$g = Ae^{-h\varphi}$$

is set, and it can be justified as follows. Replace in the equality $\int dm = \int dM$ this value for g and also divide the values (4) and (5) for dM and dm by $TaAdX_1 dY_1 \ldots dW_r$ to obtain

$$\int\int \ldots e^{-h(\varphi+\varphi^*)}\omega \cdot D \cdot d\Xi_1 dH_1 \ldots dY = \int\int e^{-h(\Phi+\Phi^*)}\Omega \cdot d\Xi_1 dH_1 \ldots dY$$

or because of the equation (3)

$$\int\int \ldots e^{-h(\varphi+\varphi^*)}\Omega \cdot d\Xi_1 dH_1 \ldots dY = \int\int e^{-h(\Phi+\Phi^*)}\Omega \cdot d\Xi_1 dH_1 \ldots dY$$

Here all the work [potential energy] and kinetic energy involved are in φ and φ^* before the collision and in Φ and Φ^* after the collision (it is possible to express

the variables $x_1, y_1, \ldots$ as functions of $X_1, Y_1, \ldots$, and on the other hand Φ and Φ^* and again $x_1, y_1, \ldots$ interchanged with $X_1, Y_1, \ldots$).

Here φ and φ^* include the kinetic energy and the work [potential energy] that do not change in the collision so that in general $\varphi + \varphi^* = \Phi + \Phi^*$ hence also both integrals in formula (6) are equal, because the function inside the integral signs are equal for all values of the integration variables. The value adopted for g fulfills in fact the condition $\int dm = \int dM$ and consequently also the time, while some state of the body is in the region (A) of formula (1). Because in this formula g has in fact those values. (There just the constant A has been suitably determined).

But now I have already in the work [Boltzmann, 1871b, #18] shown that a distribution of states given through formula (1) will not be changed in the motion of the atoms without collisions; therefore the probability of the different states of the body will also still be given by formula (1) even if it does not hold the assumption of collisions so frequent that the motion of the atoms without collisions is not influent. The formula (1) remains even valid is the collisions should so develop that the simultaneous collisions of several molecules can be neglected. By the way this teaches a difficult result that such simultaneous collisions, even if take place somewhat often, do not influence the distribution formula (1).

However in bodies which in nature are in contact with gases, there certainly are always such simoultaneous collisions; but in the parts of the bodies, in which the collisions of several molecules happen, there are no appreciable direct interaction: consequently, in its absence, it is as if over the body a collision took place with only one molecule. We want now to suppose that the probability distribuiton of the states in a warm body, also when it is not in contact with a gas, remains the same; under this assumption formula (1) holds for any warm body and I will now show how with the same ease will follow an analytic proof of the main theorem of the mechanical theory of heat.[84]

[*(p.294-308): If the canonical distribution is accepted for a system in equilibrium with the surroundings it is possible to define and compute several averages which admit physical interpretations, like for instance temperature, pressure, volume, energy, specific heat ... $(T, p, V, U, C_v \ldots)$. Boltzmann dedicates the remaining part of the work to check that such average values obey the relations that are expected from the theory of thermodynamics, i.e. they define a thermodynamic analogy or model of thermodynamics: a notion that will be formalized later. He first studies a process in which the parameters of the canonical ensemble vary,*

[84] *This is the important claim that assuming the canonical distribution for any system the main heat theorem $\oint \frac{dq}{T} = 0$ follows as well as all the main formulae of thermodynamics. For this reason it has been sometimes claimed that Boltzmann abandoned the dynamical derivation of the heat theorem: however it should be kept in mind that the basis of the discussion is the indentity between the the probability of a state (i.e. microscopic configuration) and the frequency of visit to the parallelepipedal cell defining it: for an isolated system this is of course the ergodic hypothesis which in this form is already present in the earlier works in which it is shown that this assumption implies a canonical distribution for subsystems, [Boltzmann, 1868a, 1871b,c,d, 1868-71].*

and defines the amount of heat δQ that enters in the system and the amount of work δW that the system performs on the external bodies (e.g. through the volume variation) and checks that $\frac{\delta Q}{T}$ is a two paramenters exact differential: he fulfills, at the same time, the promise made to Clausius in the priority paper that he will take into acount the variation of the external potential. Furthermore he shows that even the microcanonical distribution has the same property that the natural definition of $\frac{\delta Q}{T}$ in a process is an exact differential.
However it is hard to understand the need of the long analysis preceding p.294 and translated above. The canonical distribution was derived already in [Boltzmann, 1868a, #5] for the first time in general, as stressed in [Maxwell, 1879] quoted above, and again in [Boltzmann, 1871b, #18] with special assumptions on the density and free flight time, and again in [Boltzmann, 1871c, #19]. Once the canonical distribution is accepted the analysis from (p.294-308) can be performed.
The derivation will be reproduced in the later paper [Boltzmann, 1884, #73] and in AppendixJ, p.87 below. Therefore in this paper the theory of the equilibrium ensembles is essentially fully developed.]

H Irreversibility: Loschmidt and "Boltzmann's sea"

Quotes and comments on: *Bemerkungen über einige Probleme der mechanischen Wärmetheorie*, 1877, [Boltzmann, 1877a, #39,p.112-148].

[*Sec.I deals with problems about specific heat of liquid droplets in saturated vapors. Again there is some overlapping of part of Sec.I with Clausius' work as pointed out at footnote*[1]*, p.116.*
In Sec.II the discussion is really about a deep and clear interpretation of the second law and of the conflict between irreversibility and microscopic reversibility.
And Sec.III deals with the example of one dimensional motions to illustrate the heat theorem (a simple case is described in Sec.5 above): the example was discussed also in earlier papers of Boltzmann but this is particularly important as it introducesformally the notion of model of thermodynamics, which will be the basis of the theory of the ensembles in the 1884 work, see AppendixJ, on monocyclic systems.]

§II. On the relation between a general mechanics theorem and the second main theorem of the theory of heat (p.116)

In his work on the states of thermal equilibrium of a system of bodies, with attention to the force of gravity, Loschmidt formulated an opinion, according to which he doubts about the possibility of an entirely mechanical proof of the second theorem of the theory of heat. With the same extreme sagacity he suspects that for the correct understanding of the second theorem an analysis of

its significance is necessary, deeper than what appears indicated in my philosophical interpretation, in which perhaps various physical properties are found which are still difficult to understand, hence I shall immediately here undertake their explanation with other words.

We want to explain in a purely mechanical way the law according to which all natural processes proceed so that

$$\int \frac{dQ}{T} \leq 0$$

and so, therefore, behave bodies consistent of aggregates of point masses. The forces acting between these point masses are imagined as functions of the relative positions of the points. If they are known as functions of these relative positions we say that the interaction forces are known. Therefore the real motion of the point masses and also the transformations of the state of the body will be known once given the initial positions and velocities of the generic point mass. We say that the initial conditions must be given.

We want to prove the second theorem in mechanical terms, founding it on the nature of the interaction laws and without imposing any restriction on the initial conditions, knowledge of which is not supposed. We look also for the proof that, always whatever may be the initial conditions, the transformations of the body always take place so that

$$\int \frac{dQ}{T} \leq 0$$

Suppose now that the body is constituted by a collection of point-like, or virtually such, masses. The initial condition be so given that the successive transformation of the body proceed so that

$$\int \frac{dQ}{T} \leq 0$$

We want to claim immediately that, provided the forces stay unchanged, it is possible to exhibit another initial condition for which it is

$$\int \frac{dQ}{T} \geq 0.$$

We can consider the values of the velocities of all point masses reached at a given time t_1 and we now want to consider, instead of the preceding initial conditions, the following: at the beginning all point masses have the same positions reached, starting form the preceding initial conditions, in time t_1 but with all velocities inverted. In such case we want to remark that the evolution of the state towards the future retraces exactly the preceding evolution towards the time t_1.

It is clear that the point masses retrace the same states followed by the preceding initial conditions, but in the opposite direction. We shall see the initial state that before we had at time 0 to be realized at time t_1 [*with opposite velocities*]. Hence if before it was

$$\int \frac{dQ}{T} \leq 0$$

we shall have now ≥ 0.

On the sign of this integral the interaction cannot have influence, but it only depends on the initial conditions. In all processes in the world in which we live, experience teaches us this integral to be ≤ 0, and this is not implicit in the interaction law, but rather depends on the initial conditions. If at time 0 the state [*of the velocities*] of all the points of the Universe was opposite to the one reached after a very long time t_1 the evolution would proceed backwards and this would imply

$$\int \frac{dQ}{T} \leq 0$$

Every experimentation on the nature of the body and on the mutual interaction law, without considering the initial conditions, to check that

$$\int \frac{dQ}{T} \leq 0$$

would be vain. We see that this difficulty is very attractive and we must consider it as an interesting sophism. To get close to the fallacy that is in this sophism we shall immediately consider a system of a finite number of point masses, which is isolated from the rest of the Universe.

We think to a very large, although finite, number of elastic spheres, which are moving inside a container closed on every side, whose walls are absolutely still and perfectly elastic. No external forces be supposed acting on our spheres. At time 0 the distribution of the spheres in the container be assigned as non uniform; for instance the spheres on the right be denser than the ones on the left and be faster if higher than if lower and of the same order of magnitude. For the initial conditions that we have mentioned the spheres be at time t_1 almost uniformly mixed. We can then consider instead of the preceding initial conditions, the ones that generate the inverse motion, determined by the initial conditions reached at time t_1.

Then, as time evolves, the spheres come back; and at time t_1 will have reached a non uniform distribution although the initial condition was almost uniform. We then must argue as follows: a proof that, after the time t_1 the mixing of the spheres must be with absolute certainty uniform, whatever the initial distribution, cannot be maintained. This is taught by the probability itself; every non uniform distribution, although highly improbable, is not absolutely impossible. It is then clear that every particular uniform distribution, that follows an initial datum and is reached in a given time is as improbable as any other even if not uniform; just as in the lotto game every five numbers are equally probable as the five $1, 2, 3, 4, 5$. And then the greater or lesser uniformity of the distribution depends on the greater size of the probability that the distribution becomes uniform, as time goes.

It is not possible, therefore, to prove that whatever are the initial positions and velocities of the spheres, after a long enough time, a uniform distribution

is reached, nevertheless it will be possible to prove that the initial states which after a long enough time evolve towards a uniform state will be infinitely more than those evolving towards a nonuniform state, and even in the latter case, after an even longer time, they will evolve towards a uniform state.[85]

Loschmidt's proposition teaches also to recognize the initial states that really at the end of a time t_1 evolve towards a very non uniform distribution; but it does not imply the proof that the initial data that after a time t_1 evolve into uniform distributions are not infinitely many more. Contrary to such statement is even the proposition itself which enumerates as infinitely many more uniform distributions than non uniform, and the number of the states which, after a given time t_1 arrive to uniform distribution must also be much larger than those which arrive to nonuniform distributions, and these are just the configurations that arise in the initial states of Loschmidt becoming non uniform at time t_1.

It is actually possible to calculate the ratio of the numbers determining the probabilities of the different initial states, perhaps leading to "an interesting method to calculate the thermal equilibria"[86] exactly analogous to the one that leads to the second theorem. It is at least in some special cases successfully checked when a system undergoes a transformation from a nonuniform state to a uniform one, then $\int \frac{dQ}{T}$ will be intrinsically negative, while it will be positive in the inverse case. Since there are infinitely many more uniform than nonuniform distributions of the states, therefore the last case will be extremely improbable: and in practice it could be considered impossible that at the beginning a mixture of oxygen and nitrogen are given so that after one month the chemically pure oxygen is found in the upper part while the nitrogen is in the lower, an event that probability theory states as improbable but not as absolutely impossible.

Nevertheless it seems to me that the Loschmidtian theorem has a great importance, since it tells us how intimately related are the second principle and the calculus of probabilities. For all cases in which $\int \frac{dQ}{T}$ can be negative it is also possible to find an initial condition very improbable in which it is positive. It is clear to me that for closed atomic trajectories $\int \frac{dQ}{T}$ must always vanish. For non closed trajectories it can also be negative. Now a peculiar consequence of the Loschmidtian theorem which I want to mention here, *i.e.* that the state of the Universe at an infinitely remote time, with fundamentally equal confidence, can be considered with large probability both as a state in which all temperature differences have disappeared, and as the state in which the Universe will evolve in the remote future.[87]

This is analogous to the following case: if we want that, in a given gas at a given time, a non uniform distribution is realized and that the gas remains for a very long time without external influences, then we must think that as the distribution of the states was uniform before so it will become again entirely

[85] *Today this important discussion is referred as the argument of Boltzmann's sea, [Uhlenbeck, 1968].*

[86] *The idea will be implemented in [Boltzmann, 1877b, #42], see AppendixI.*

[87] *Reference to the view of Clausius who claims that in the remote future the Universe will be in an absolutely uniform state. Here Boltzmann says that the same must have happened, with equal likelihood in the remote past.*

uniform.

In other words: as any nonuniform distribution evolves at the end of a time t_1 towards a uniform one the latter, if inverted, as the same time t_1 elapses again comes back to the initial nonuniform distribution (precisely for the said inversion). The [*new*] but inverted initial condition, chosen as initial condition, after a time t_1 similarly will evolve to a uniform distribution.[88]

But perhaps such interpretation relegates in the domain of probability theory the second principle, whose universal use appears very questionable, and nevertheless just because of the theory of probability it will be realized in every laboratory experimentation.

[§*III, p.127 and following: a check of the heat theorem is presented in the case of a central motion, which will be revisited in the papers of 1884 by v. Helmholtz and Boltzmann. The cases of central motion with a repulsive potential* $\frac{b}{r^2}$ *plus either a gravitational potential or a harmonic potential are treated in great detail.*
The result is again that $\frac{\delta Q}{T}$ *is an exact differential only if the potential* $\delta b = b = 0$*, see also [Gallavotti, 2014, p.205] and [Gallavotti, 2000, p.45].*
The main purpose and conclusion of Sec. III seems however to be that when there are several constants of motion (which it would be tempting to consider parameters of the states of the system) it cannot be expected that the average kinetic energy is an integrating factor for $dQ = dE - \langle\, \partial_{\mathbf{c}}\varphi \cdot \delta\mathbf{c}\,\rangle$*. The Newtonian potential is a remarkable exception. Other exceptions are the* 1*–dimensional systems, obtained as special cases of the central potentials cases with zero area velocity,* $\beta \equiv 0$*. Several special one-dimensional cases associated with* 2*-dimensional central motions are considered: the matter will be discussed a few years laterin [Helmholtz, 1895a,b], and immediately afterwards in [Boltzmann, 1884, #73], leading to a general theory of the ensembles.*]

I Discrete phase space, count of its points and entropy.

Quotes and comments on: Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung, respektive den Sätzen über das Wärmegleichgewicht, 1877, [Boltzmann, 1877b, #42,p.164-233].

[*This work takes up the method already used in [Boltzmann, 1868a, #5] of dividing phase space into cells to count the number of microscopic states: implementing the statement, in [Boltzmann, 1877a, #39,p.121], that the count is possible and may lead to an interesting method to calculate the thermal equilibria. The results will be later, by other authors, summarized in the formula*

[88] *I.e.if once having come back we continue the evolution for as much time again a uniform distribution is reached.*

$S = k_B \log N$, N being the number of ways of realizing the microscopic configurations which assign to few thermodynamic observables value equal to their averages, in systems with many particles. In the 1868 work phase space was simply discretized and the microcanonical distribution derived (in Sec.III) by assuming that all cells, in the $(6N-1)$-dimensional phase space, which could be visited were indeed visited and the frequency of visit was assumed equal to the number of ways the cells could be occupied so that the total energy has the fixed value.
The novelty is that Boltzmann uses the combinatorial count details to consider the probabilities of all configurations and shows that just the ones that maximize the frequency of visit are by far sufficient to compute the averages of thermodynamic observables. That played an important role in the work that he had to do to defend and clarify his ideas and results.
To perform the count the energy is supposed to take values regularly spaced and with a degeneracy depending on the space dimensionality. Hence it is imagined that the momentum space is divided into small cubic cells of sides dc; the ones in which the speed is in the shell between $e = k\varepsilon$ and $e + de$ (with ε the size of the discrete kinetic energy jumps and $k \geq 0$ integer) or speed between c and $c + dc$, with $c = \sqrt{\frac{2k\varepsilon}{m}}$, is $\frac{4\pi}{m} cde = 4\pi c^2 dc$, i.e. it is proportional to $c^2 dc$, while in dimension 2 it is proportional to dc and in 1 dimension it is just the constant 2 corresponding to $\pm c$.
At the end of the work also the positions are considered and the cells become parallelepipeds in phase space: however the forces considered are only external forces and the system is still a low density gas.
It should be remarked that although the general strategy is very clear, and the role of discreteness is stressed and used to give a new definition and interpretation of entropy, the analysis is closely related, less general but much more detailed and withnew perspectives, like entropy even out of equilibrium, with respect to the early work [Boltzmann, 1868a, #5]. There, in Sec.II. cells were constructed in momentum space and in Sec.III in phase space, i.e. were parallelepipeds in a regular lattice in phase space, see AppendixC above. And mainly the system was not a rarefied gas but the internal forces were rather general conservative forces, as stressed by Maxwell, [Maxwell, 1879].
It seems that this restriction on the forces, not commented by Boltzmann, reflects his intention to connect the combinatorial work with the Boltzmann equation and the related H-theorem.]

p.166 ... We now wish to solve the problem which on my above quoted paper *Bemerkungen über einige Probleme der mechanischen Wärmetheorie*, [Boltzmann, 1877a, #39], I have already formulated clearly, *i.e.* the problem of determining the "ratios of the number of different states of which we want to compute the probabilities".

We first want to consider a simple body, *i.e.* a gas enclosed between absolutely elastic walls and whose molecules are perfect spheres absolutely elastic (or centers of force which, now, interact only when their separation is smaller

than a given quantity, with a given law and otherwise not; this last hypothesis, which includes the first as a special case does not at all change the result). Nevertheless in this case the use of probability theory is not easy. The number of molecules is not infinite in a mathematical sense, although it is extremely large. The number of the different velocities that every molecule can have, on the contrary, should be thought as infinite. Since the last fact renders much more difficult the calculations, thus in the first Section of this work I shall rely on easier conceptions to attain the aim, as I often did in previous works (for instance in the *Weiteren Studien*, [Boltzmann, 1872, #22]).

.....

§I. The number of values of the kinetic energy is discrete.(p.167)

We want first to suppose that every molecule can assume a finite number of velocities, for instance the velocities

$$0, \frac{1}{q}, \frac{2}{q}, \frac{3}{q}, \ldots, \frac{p}{q},$$

where p and q are certain finite numbers. At a collision of two molecules will correspond a change of the two velocities, so that the state of each will have one of the above mentioned velocities, *i.e.*

$$0, \text{ or } \frac{1}{q}, \text{ or } \frac{2}{q}, \ \&tc \ \textit{until} \ \frac{p}{q},$$

It is plain that this fiction is certainly not realized in any mechanical problem, but it is only a problem that is much easier to treat mathematically, and which immediately becomes the problem to solve if p and q are allowed to become infinite.

Although this treatment of the problem appears too abstract, also it very rapidly leads to the solution of the problem, and if we think that all infinite quantities in nature mean nothing else than going beyond a bound, so the infinite variety of the velocities, that each molecule is capable of taking, can be the limiting case reached when every molecule can take an always larger number of velocities.

We want therefore, temporarily, to consider how the velocities are related to their kinetic energy. Every molecule will be able to take a finite number of values of the kinetic energy. For more simplicity suppose that the values of the kinetic energy that every molecule can have form an arithmetic sequence,

$$0, \varepsilon, \ 2\,\varepsilon, \ 3\,\varepsilon, \ldots, p\,\varepsilon$$

and we shall denote with P the largest of the possible values of p.

At a collision each of the two molecules involved will have again a velocity

$$0, \text{ or } \varepsilon, \text{ or } 2\,\varepsilon, \text{ etc.}\ldots, \ p\,\varepsilon,$$

and in any case the event will never cause that one of the molecules will end up with having a value of the kinetic energy which is not in the preceding sequence.

Let n be the number of molecules in our container. If we know how many molecules have a kinetic energy zero, how many ε, &tc, then we say that the distribution of the kinetic energy between the molecules is given.

If at the initial time a distribution of the molecules states is given, it will in general change because of the collisions. The laws under which such changes take place have been often object of research. I immediately remark that this is not my aim, so that I shall not by any means depend on how and why a change in the distribution takes place, but rather to the probability on which we are interested, or expressing myself more precisely, I will search all combinations that can be obtained by distributing $p+1$ values of kinetic energy between n molecules, and hence examine how many of such combinations correspond to a distribution of states. This last number gives the probability of the relevant distribution of states, precisely as I said in the quoted place of my *Bemerkungen über einige Probleme der mechanischen Wärmetheorie* (p.121), [Boltzmann, 1877a, #39].

Preliminarily we want to give a purely schematic version of the problem to be treated. Suppose that we have n molecules each susceptible of assuming a kinetic energy

$$0, \varepsilon,\ 2\varepsilon,\ 3\varepsilon, \ldots, p\varepsilon.$$

and indeed these kinetic energy will be distributed in all possible ways between the n molecules, so that the sum of all the kinetic energy stays the same; for instance is equal to $\lambda\varepsilon = L$.

Every such way of distributing, according to which the first molecule has a given kinetic energy, for instance 2ε, the second also a given one, for instance 6ε, &tc until the last molecule, will be called a "complexion", and certainly it is easy to understand that each single complexion is assigned by the sequence of numbers (obviously after division by ε) to which contribute the kinetic energy of the single molecules. We now ask which is the number $\mathcal{B}$ of the complexions in which w_0 molecules have kinetic energy 0, w_1 kinetic energy ε, w_2 kinetic energy 2ε, *&tc*, ... w_p kinetic energy $p\varepsilon$. [89]

We have said before that when is given how many molecules have zero kinetic energy, how many ε *&tc*, then the distribution of the states among the molecules is given; we can also say: the number $\mathcal{B}$ gives us how many complexions express a distribution of states in which w_0 molecules have zero kinetic energy, w_1 kinetic energy ε, *&tc*, or it gives us the probability of every distribution of states. Let

[89] The word "complexion", defined here, is no longer often employed: here it denotes a partition of the total kinetic energy defined by the number of particles, out of a total of n, that have the same kinetic energy. It can also denote, more generally, the partition of the total kinetic energy of the particles that occupy distinct volume elements ds around points q in R^{3n}, *i.e.* assigning for each volume element ds the number of particles that have kinetic energy $n\kappa - \chi(q)$, if $n\kappa$ is the *total energy* and $\chi(q)$ the potential energy, as in the derivation of the microcanonical ensemble in [Boltzmann, 1868a, #5,p.95,l.-6] (where, however, it was not given a special name). In the latter sense it is now called a "microstate" or a "microscopic configuration" in the n-particles phase space R^{6n}.

us divide in fact the number $\mathcal{B}$ by the total number of all possible complexions and we get in this way the probability of such state.

It does not follow from here that the distribution of the states gives which are the molecules which have a given kinetic energy, but only how many they are, so we can deduce how many (w_0) have zero kinetic energy, and how many (w_1) among them have one unit of kinetic energy ε, *&tc.* All of those values zero, one, *&tc* we shall call elements of the distribution of the states.

(p.170) ..... (p.175)

We shall first treat the determination of the number denoted above $\mathcal{B}$ for each given distribution of states, *i.e.* the permutability of such distribution of states. Then denote by J the sum of the permutabilities of all possible distributions of states, and hence the ratio $\frac{\mathcal{B}}{J}$ gives immediately the probability of the distribution that from now on we shall always denote W.

We also want right away to calculate the permutability $\mathcal{B}$ of the distributions of states characterized by w_0 molecules with zero kinetic energy, w_1 with kinetic energy ε *&tc.* Hence evidently

$$w_0 + w_1 + w_2 + \ldots + w_p = n \tag{1}$$

$$w_1 + 2w_2 + 3w_3 + \ldots + pw_p = \lambda, \tag{2}$$

and then n will be the total number of molecules and $\lambda\varepsilon = L$ their kinetic energy.

We shall write the above defined distribution of states with the method described, so we consider a complexion with w_0 molecules with zero kinetic energy, w_1 with unit kinetic energy *&tc.* We know that the number of permutations of the elements of this complexion, with in total n elements distributed so that among them w_0 are equal between them, and so w_1 are equal between them ... The number of such complexions is known to be[90]

$$\mathcal{B} = \frac{n!}{(w_0)!\,(w_1)!\ldots} \tag{3}$$

The most probable distribution of states will be realized for those choices of the values of $w_0, w_1, \ldots$ for which $\mathcal{B}$ is maximal and quantities $w_0, w_1, \ldots$ are at the same time constrained by the conditions (1) and (2). The denominator of $\mathcal{B}$ is a product and therefore it will be better to search for the minimum of its logarithm, *i.e.* the minimum of

$$M = \ell[(w_0)!] + \ell[(w_1)!] + \ldots \tag{4}$$

where ℓ denotes the natural logarithm.

.....

[*Follows the discussion of this simple case in which the energy levels are not degenerate (i.e. this is essentially a 1-dimensional case) ending with the Maxwell distribution of the velocities.*]

[90] *Here particles are considered distinguishable and the total number of complexions is* P^n.

Sec.II, *The kinetic energies contuinously permute each other*, (p.186)
[*Boltzmann goes on to consider the case of* 2*-dimensional and of* 3*–dimensional cells (of sides* da, db *or* da, db, dc*) in the space of the velocities (to be able to take degeneracy into account), treating first the discrete case and then taking the continuum limit: getting the canonical distribution. The system considered is a very rarefied collection of molecules whose state is simply characterized by the value of the velocity coordinates each of which is a multiple of a small quantity* ε*. Hence, see formulae (30),(31), at p.191, the cells in momentume space as small cubes of side* ε*.*]
Sec.III, *Consideration of polyatomic molecules and external forces* , (p.198)
[*Deals with the case of polyatomic molecules and external forces. Therefore it becomes necessary also to consider the discretization of position space (of the molecules atoms with respect to their center of mass), and if there is also an external force (gravity is considered) it becomes necessary to consider, and discretize, for each molecule also the baricenter coordinates.*]
Sec.IV, *On the conditions on the maximal exponent values in the free products in the function determining the distribution of states*, (p.204)
[*Studies the maximum value of the product* $\prod_{i=1}^{p} w_i$ *under the conditions that* $\sum_{i=1}^{p} w_i = n$ *and* $\varepsilon \sum_{i=1}^{p} i\, w_i = L$ *(at given* n, ε, L *aiming at* $n \to \infty, L/n = const, \varepsilon \to 0$*).*
An accurate analysis of the combinatorics developed in this paper, together with [Boltzmann, 1868a, #5], is in [Bach, 1990] where two ways of computing the distribution when the energy levels are discrete are discussed pointing out that unless the continuum limit, as considered by Boltzmann in the two papers, was taken would lead to a distribution of Bose-Einstein type or of Maxwell-Boltzmann type: [Gallavotti, 2000, Sec.(2.2),(2.6)].]
Sec.V, *Relation between entropy and the quantities that I have introduced as probability distributions*, (p.215),
[*The link between the probability distributions found in the previous sections with entropy is discussed, dealing with examples derived through the combinatorial analysis of the previous sections, and expressing it through the "permutability"* Ω *(i.e. the count of the possible states). Examples are computation of the free gas entropy, the entropy change expansion of a free gas in a half empty container, the entropy of a free gas in the gravity field (barometric formula).*
On p.218 the following celebrated statement is made (in italics in the original) about "permutability" (i.e. number of ways in which a given (positions-velocities) distribution can be achieved) and is illustrated with the example of the expansion of a gas in a half empty container:]

Let us think of an arbitrarily given system of bodies, which undergo an arbitrary change of state, without the requirement that the initial or final state be equilibrium states; then always the measure of the permutability of all bodies involved in the transformations continually increases and can at most remain constant, until all bodies during the transformation are found with infinite ap-

proximation in thermal equilibrium.[91]

[*The last comment underlines that the new view of entropy is not restricted to equilibrium states: it makes sense as a "Lyapunov function" also in the evolution towards equilibrium; Klein remarks:*] "*...* $\log P$ *was well defined whether or not the system is in equilibrium, so that it could serve as a suitable generalization of entropy*", [Klein, 1973, p.82].

J Monocyclic and orthodic systems. Ensembles

Quotes and comments on: Über die Eigenshaften monozyklischer und anderer damit verwandter Systeme", 1884, [Boltzmann, 1884, #73,p.122-152].

[*Thermodynamic analogies are fully discussed starting with the works of Helmoltz to whom the notion, and examples, are attributed by Boltzmann although he (as well as Clausius) had already several times employed them, even though without a formal definition, [Boltzmann, 1866, Clausius, 1871],[Boltzmann, 1877a, #39,p.127-148]. Boltzmann goes far beyond Helmoltz and fully develops the theory of ensembles, which had been left at an early stage since his first works [Boltzmann, 1868a, 1871b,c, 1868-71].*]

The most complete proof of the second main theorem is manifestly based on the remark that, for each given mechanical system, equations that are analogous to equations of the theory of heat hold.[92] But, on the one hand, it is evident that the proposition, in this generality, cannot be valid and, on the other hand, because of our scarce knowledge of the so called atoms, we cannot establish the exact mechanical properties with which the thermal motion manifests itself: hence the task arises to search in which cases and up to which point the equations of mechanics are analogous to the ones of the theory of heat. We should not refrain to list the mechanical systems with behavior congruent to the one of the warm bodies, rather than to look for all systems for which it is possible to establish stronger or weaker analogies with warm bodies. The question has been posed in this form by Mr. von Helmoltz [93] and I have aimed, in what follows and before proceeding to general propositions, to treat a very special case,of the analogy that he discovered between the thermodynamic behavior and that of systems, that he calls monocyclic, and to follow the propositions, to which I will refer, of the mechanical theory of heat intimately related to monocyclic systems. [94]

[91] *After the last word appears in parenthesis and still in italics (reversible transformations), which seems to mean "or performing reversible transformations".*

[92] *italics added; see Sec.10 for the notions of thermodynamic analogies or thermodynamics models.*

[93] Berl.Ber, 6 and 27 March 1884.

[94] A very general example of monocyclic system is offered by a current without resistance (see Maxwell, "Treatise on electricity", Sec.579-580, [p.224-225], where x and y represent the v. Helmholtzian p_a and p_b).

§1

Let a point mass move, according to Newton's law of gravitation, around a fixed central fixed body O, on an elliptic trajectory. Motion is not in this case monocyclic; but it can be made such with a trick, that I already introduced in the first Section of my work "*Einige allgemeine sätze über Wärmegleichgewicht*"[95] and that also Maxwell [96] has again followed.

Imagine that the full elliptic trajectory is filled with mass, which at every point has a density (of mass per unit length) such that, while time elapses, density in each point of the trajectory remains unchanged. As it would be a Saturn ring thought as a homogeneous flow or as a homogeneous swarm of solid bodies so that, fixed one of the rings among the different possible ones a stationary motion would be obtained. The external force can accelerate the motion or change its eccentricity; this can be obtained increasing or diminishing slowly the mass of the central body, so that external work will be performed on the ring which, by the increase or diminution of the central body mass, in general is not accelerated nor decelerated in the same way. This simple example is treated in my work *Bemerkungen über einige Probleme der mechanischen Wärmetheorie*[97] where in Section 3 are derived formulae in which now we must set $b = 0$ and for m we must intend the total mass of the considered ring

...

[*Detailed comparison with the work of Helmoltz follows. A monocyclic system is imagined to have its orbits filled with points with a density proportional to the time spent in its arcs (here the example of the Saturn rings is evoked). Varying the parameters of the orbit the state changes (i.e. the orbit changes). Various examples of monocyclic systems are worked out: for all of their periodic orbits is defined the amount of heat dQ that the system receives in a transformation ("work to increase the internal motion" or "infinitesimal direct increment" of the internal motion, i.e. the heat acquired by a warm body), and the amount of work dW that the system does against external forces as well as the average kinetic energy L; in all examples it is shown that* $\frac{dQ}{L}$ *is an exact differential. This leads Boltzmann to generalize the Helmoltz' conception of state of a monocyclic system, i.e. of a priodic orbit with an invariant density. The generalization is that of "monode" for a system whose states are imagined as regions of phase space filled with a density that is invariant under the time evolution. Thus a monode is a nice word to indicate an invariant (normalized) distribution on phase space. If the points of a monode are evolved with the equations of motion the density invariance (or stationarity) implies that they will look the same forever (hence their name). In a discrete phase space a monode will consist of*

[95] Wiener. Berl. **63**, 1871, [Boltzmann, 1871b, #18], [*see also [Gallavotti, 2000, Sec.1A.1].*]

[96] Cambridge Phil. Trans. **12**, III, 1879 (see also Wiedemanns Beiblätter, **5**, 403, 1881).

[97] Wien, Ber. **75**. See also Clausius, Pogg. Ann. **142**, 433; Math. Ann. von Clebsch, **4**, 232, **6**, 390, Nachricht. d. Gött. Gesellsch. Jarhrg. 1871 and 1871; Pogg. nn. **150**, 106, and Ergängzungs, **7**,215.

points each representing a possible microscopic configuration. Of course there are many such monodes and in the following Boltzmann will collect them into distinguished families generating important definitions (p.129-130):]

§2, (p.129)

...
I would permit myself to call systems whose motion is stationary in this sense with the name *monodes*. [98] They will therefore be characterized by the property that in every point persists unaltered a motion, not function of time as long as the external forces stay unchanged, and also in no point, in no region nor through any surface mass or kinetic energy enters from the outside or goes out. If the kinetic energy is the integrating denominator of the differential dQ, which directly gives the work to increase the internal motion, [99] then I will say that the such systems are *orthodes*. ....
[*Etymologies:* monode=μόνος+εἶδος=unique+aspect; orthode=ὀρθός+ εἶδος= right + aspect.

The notion of monode and orthode will be made more clear in the next subsection 3. It is already clear that while the monode is just a stationary distribution on phase space an orthode must be a collection of monodes indexed by parameters that can be varied, to represent processes consisting in varying the parameters so it can be checked that the collection (or "ensemble") is a model of thermodynamics, i.e. it is "orthodic" or generates a thermodynamic analogy.]

§3. (p.131)

After these introductory examples I shall pass to a very general case. Consider an arbitrary system, whose state is characterized by arbitrary coordinates $p_1, p_2, \ldots, p_g$; and let the corresponding momenta be $r_1, r_2, \ldots, r_g$. For brevity we shall denote the coordinates by $p_{\mathbf{g}}$ and the momenta by $r_{\mathbf{g}}$. Let the internal and external forces be also assigned; the first be conservative. Let ψ be the kinetic energy and χ the potential energy of the system, then also χ is a function of the $p_{\mathbf{g}}$ and ψ is a homogeneous function of second degree of the $r_{\mathbf{g}}$ whose coefficients can depend on the $p_{\mathbf{g}}$. The arbitrary constant appearing in χ will be determined so that χ vanishes at infinite distance of all masses of the system or even at excessive separation of their positions. We shall not adopt the restrictive hypothesis that certain coordinates of the system be constrained to assigned values, hence also the external forces will not be characterized other than by their almost constancy on slowly varying parameters. The more so the slow variability of the external forces will have to be taken into account either because χ will become an entirely new function of the coordinates $p_{\mathbf{g}}$, or because some constants that appear in χ, which we shall indicate by $p_{\mathbf{a}}$, vary slowly.

[98] With the name "stationary" Mr. Clausius would denote every motion whose coordinates remain always within a bounded region.

[99] *In an infinitesimal transformation, i.e. variation of internal energy summed to work done by the system on the outside, defines the heat received by the system.*

1. We now imagine to have a large number N of such systems, of exactly identical nature; each system absolutely independent from all the others.[100] The number of such systems whose coordinates and momenta are between the limits p_1 and $p_1 + dp_1$, p_2 and $p_2 + dp_2 \ldots$, r_g and $r_g + dr_g$ be

$$dN = Ne^{-h(\chi+\psi)} \frac{\sqrt{\Delta}\, d\sigma\, d\tau}{\int\int e^{-h(\chi+\psi)}\sqrt{\Delta}\, d\sigma\, d\tau},$$

where $d\sigma = \Delta^{-\frac{1}{2}} dp_1 dp_2 \ldots dp_g$, $d\tau = dr_1\, dr_2 \ldots dr_g$ (for the meaning of Δ see Maxwell *loc. cit* p.556).[101]

The integral must be extended to all possible values of the coordinates and momenta. The totality of these systems constitute a *monode* in the sense of the definition given above (see, here, especially Maxwell *loc. cit.*) and I will call this species of monodes with the name *holodes*, [Etymology: ὅλος="global"+εἶδος="aspect"]. [102]

Each system I will call an *element* of the holode. [103] The total kinetic energy of a holode is[104]

$$L = \frac{Ng}{2h}.$$

Its potential energy Φ equals N times the average value $\overline{\chi}$ of χ, *i.e.* :

$$\Phi = N\frac{\int \chi\, e^{-h\chi}\, d\sigma}{\int e^{-h\chi}\, d\sigma}.$$

---

[100] *In modern language this is sometimes an ensemble: it is the generalization of the Saturn ring of Sec.1: each representative system is like a stone in a Saturn ring. It is a way to realize all states of motion of the same system. Their collection does not change in time and keeps the same aspect, if the collection is stationary, i.e. is a "monode".*

[101] In general the kinetic energy is a quadratic form in the $r_{\mathbf{g}}$ and then Δ is its determinant: it is the Jacobian of the linear transformation $r_{\mathbf{g}} \longleftrightarrow r'_{\mathbf{g}}$ that brings the kinetic energy in the form $\frac{1}{2}|r'_{\mathbf{g}}|^2$.

[102] *Probably because the canonical distribution deals with all possible states of the system and does not select quantities like the energy or other constants of motion.*

[103] *Summarizing: a monode is a probability distribution; the monodes so defined are a special class of distributions each of which is called a holode. The holodes depend on parameters, h, V in this case, and it makes sense to ask whether they provide a thermodynamic analogy: i.e. if they are "orthodic".*

[104] *In the case of a gas the number g must be thought as the Avogadro's number times the number of moles, while the number N is a number much larger and equal to the number of cells which can be thought to constitute a regular discretization of the phase space. Its introduction is not necessary for the purpose of defining models of thermodynamics, and Boltzmann already in 1868 and 1871 had treated canonical and microcanonical distributions with $N = 1$: it seems that the introduction of the N copies, adopted later also by Gibbs, intervenes for ease of comparison of the work of v. Helmholtz with the preceding theory of 1871. Remark that Boltzmann accurately avoids to say too explicitly that the work of v. Helmholz is, as a matter of fact, a different and particular version of his preceding work. Perhaps this is explained by the caution of Boltzmann who in 1884was thinking to move to Berlin, solicited and supported by v. Helmholtz. We also have to say that the works of 1884 by v. Helmholtz became an occasion for Boltzmann to review and systematize his own works on the heat theorem which, after the present work, took up the form and the generality that we still use today as "theory of the statistical ensembles".*

The coordinates $p_{\mathbf{g}}$ correspond therefore to the v. Helmholtzian $p_{\mathbf{b}}$, which appear in the kinetic energy ψ and potential energy χ of an element. The intensity of the motion of the entire ergode[105] and hence also L and Φ depend now on h and on $p_{\mathbf{a}}$, as for Mr. v. Helmholtz on $q_{\mathbf{b}}$ and $p_{\mathbf{a}}$.

The work provided for a direct increase, see p.84, of internal motion is:

$$\delta Q = \delta\Phi + \delta L - N\frac{\int \delta\chi\, e^{-h\chi}\, d\sigma}{\int\, e^{-h\chi}\, d\sigma}$$

(see here my work[106] *Analytischer Beweis des zweiten Hauptsatzes der mechanischen Wärmetheorie aus den Sätzen über das Gleichgewicht des lebendigen Kraft*), [Boltzmann, 1871c, #19]. The amount of internal motion generated by the external work, when the parameter p_a varies [107] by δp_a, is therefore $-P\delta p_a$, with

$$-P = \frac{N\int \frac{\partial\chi}{\partial p_a} e^{-h\chi}\, d\sigma}{\int e^{-h\chi}\, d\sigma}$$

The kinetic energy L is the integrating denominator of δQ: all holodes are therefore orthodic, and must therefore also provide us with thermodynamic analogies. Indeed let [108]

$$s = \frac{1}{\sqrt{h}}\Big(\int e^{-h\chi} d\sigma\Big)^{\frac{1}{g}} e^{\frac{h\chi}{g}} = \sqrt{\frac{2L}{Ng}}\Big(\int e^{-h\chi} d\sigma\Big)^{\frac{1}{g}} e^{\frac{\Phi}{2L}},$$

$$q = \frac{2L}{s}, \quad K = \Phi + L - 2L\log s, \quad H = \Phi - L,$$

[105] *This is a typo as it should be holode: the notion of ergode is introduced later in this work.*

[106] Wien. Ber., **63**, 1871, formula (17).

[107] *Here we see that Boltzmann considers among the parameters p_a coordinates such as the dimensions of the container: this is not explicitly said but it is often used in the following.*

[108] *Here the argument in the original relies to some extent on the earlier paragraphs: a self contained check is reported in this footnote for ease of the reader:*

$$F \overset{def}{=} -h^{-1}\log\int e^{-h(\chi+\varphi)} \overset{def}{=} -h^{-1}\log Z(\beta, p_a), \qquad T = h^{-1}$$

and remark that if $P \overset{def}{=} \frac{1}{h}\partial_{p_a}\log Z$

$$dF = (h^{-2}\log Z + h^{-1}(\Phi + L))dh - h^{-1}\partial_{p_a}\log Z\, dp_a = (-\frac{1}{h}F + \frac{1}{h}U)dh - Pdp_a$$

Define S via $F \overset{def}{=} U - TS$ and $U = \Phi + L$ then

$$dF = dU - TdS - SdT = -\frac{dT}{T}(-(U - TS) + U) - Pdp_a$$

hence the factor $T^{-1} = h$ is the integrating factor for $dQ \overset{def}{=} dU + Pdp_a$ because

$$dU - TdS - SdT = -\frac{dT}{T}TS - Pdp_a \;\Rightarrow\; TdS = dU + Pdp_a$$

see [Gallavotti, 2000, Eq.(2.2.7)].

[*the intermediate expression for s is not right and instead of* χ *in the exponential should have the average* $\frac{\Phi}{N}$ *of* χ]

2. Let again be given many (N) systems of the kind considered at the beginning of the above sections; let all be constrained by the constraints

$$\varphi_1 = a_1,\ \varphi_2 = a_2,\ \dots\ , \varphi_k = a_k.$$

These relations must also, in any case, be integrals of the equations of motion. And suppose that there are no other integrals. Let dN be the number of systems whose coordinates and momenta are between p_1 e $p_1 + dp_1$, p_2 and $p_2 + dp_2$, $\dots$ r_g and $r_g + dr_g$. Naturally here the differentials of the coordinates or momenta that we imagine determined by the equations $\varphi_1 = a_1, \dots$ will be missing. These coordinates or momenta missing be $p_c, p_d, \dots, r_f$; their number be k. Then if

$$dN = \frac{\frac{N dp_1 dp_2 \dots dr_g}{\sum \pm \frac{\partial \varphi_1}{\partial p_c} \dots \frac{\partial \varphi_k}{\partial r_f}}}{\int\int \dots \frac{dp_1 dp_2 \dots dr_g}{\sum \pm \frac{\partial \varphi_1}{\partial p_c} \cdot \frac{\partial \varphi_2}{\partial p_d} \dots \frac{\partial \varphi_k}{\partial r_f}}}$$

the totality of the N systems will constitute a monode, which is defined by the relations $\varphi_1 = a_1, \dots$. The quantities a can be either constant or subject to slow variations. The functions φ in general may change form through the variation of the p_a, always slowly. Each single system is again called element.

Monodes that are constrained through the only value of the equation of the kinetic energy[109] will be called *ergodes*, while if also other quantities are fixed will be called *subergodes*. The ergodes are therefore defined by

$$dN = \frac{\frac{N\, dp_1 dp_2 \dots dp_g dr_1 \dots dr_{g-1}}{\frac{\partial \psi}{\partial r_g}}}{\int\int \frac{dp_1 dp_2 \dots dp_g dr_1 \dots dr_{g-1}}{\frac{\partial \psi}{\partial r_g}}}$$

Hence for the ergodes there is a φ, equal for all the identical systems and which stays, during the motion, equal to the constant energy of each system $\chi + \psi = \frac{1}{N}(\Phi + L)$. Let us set again $\Delta^{-\frac{1}{2}} dp_1 dp_2 \dots dp_g = d\sigma$, and then (see the works cited above by me and by Maxwell):

$$\Phi = N \frac{\int \chi \psi^{\frac{g}{2}-1} d\sigma}{\int \psi^{\frac{g}{2}-1} d\sigma}, \qquad L = N \frac{\int \psi^{\frac{g}{2}} d\sigma}{\int \psi^{\frac{g}{2}-1} d\sigma},$$

$$\delta Q = N \frac{\int \delta\psi \psi^{\frac{g}{2}-1} d\sigma}{\int \psi^{\frac{g}{2}-1} d\sigma} = \delta(\Phi + L) - N \frac{\int \delta\chi\, \psi^{\frac{g}{2}-1} d\sigma}{\int \psi^{\frac{g}{2}-1} d\sigma},$$

L is again the integrating factor of δQ,[110] and the entropy thus generated is

[109] *The equation of the kinetic energy is the energy conservation* $\varphi = a$ *with* $\varphi = \psi + \chi$, *if the forces are conservative with potential* χ.

[110] *The (elementary) integrations on the variables* $r_{\mathbf{g}}$ *with the constraint* $\psi + \chi = a$ *have been explicitly performed: and the factor* $\psi^{\frac{g}{2}-1}$ *is obtained, in modern terms, performing the integration* $\int \delta(\chi + \psi - a) dr_{\mathbf{g}}$ *and in the formulae* ψ *has to be interpreted as* $a - \chi$, *as already in [Boltzmann, 1868a, 1871b, 1868-71].*

$\log(\int \psi^{\frac{g}{2}} d\sigma)^{\frac{2}{g}}$, while it will also be $\delta Q = q\,\delta s$ if it will be set:

$$s = (\int \psi^{\frac{g}{2}} d\sigma)^{\frac{1}{g}}, \qquad q = \frac{2L}{s}.$$

Together with the last entropy definition also the characteristic function $\Phi - L$ is generated. The external force in the direction of the parameter p_a is in each system

$$-P = \frac{\int \frac{\partial \chi}{\partial p_a} \psi^{\frac{g}{2}-1} d\sigma}{\int \psi^{\frac{g}{2}-1} d\sigma}.$$

Among the infinite variety of the subergodes I consider those in which for all systems not only is fixed the value of the equation of kinetic energy [*value of the energy*] but also the three components of the angular momentum. I will call such systems *planodes*. Some property of such systems has been studied by Maxwell, *loc. cit.*. Here I mention only that in general they are not orthodic.
...
The nature of an element of the ergode is determined by the parameters $p_{\mathbf{a}}$[111]. Since every element of the ergode is an aggregate of point masses and the number of such parameters $p_{\mathbf{a}}$ is smaller than the number of all Cartesian coordinates of all point masses of an element, so such $p_{\mathbf{a}}$ will always be fixed as functions of these Cartesian coordinates, which during the global motion and the preceding developments remain valid provided these functions stay constant as the kinetic energy increases or decreases. [112].
....

[*p.138: Follow more examples. The concluding remark (p.140) in Sec. 3 is of particular interest as it stresses that the generality of the analysis of holodes and ergodes is dependent on the ergodic hypothesis. However the final claim, below, that it applies to polycyclic systems may seem contradictory*]
...

(p.140)
The general formulae so far used apply naturally both to the monocyclic systems and to the polycyclic ones, as long as they are ergodic,[113] and therefore I omit to increase further the number of examples.
...

[111] *In the text, however, there is* $p_{\mathbf{b}}$*: typo?*
[112] *Among the* $p_{\mathbf{a}}$ *we must include the container dimensions* a, b, c*, for instance: they are functions of the Cartesian coordinates which, however, are trivial constant functions. The mention of the variability of the kinetic energy means that the quadratic form of the kinetic energy must not depend on the* $p_{\mathbf{a}}$*.*
[113] *It is sometimes stated that the word "ergodic" is never used by Boltzmann: here is such an instance.*

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