

# Henri Poincaré: The Status of Mechanical Explanations and the Foundations of Statistical Mechanics

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**Abstract** The first goal of this paper is to show the evolution of Poincaré's opinion on the mechanistic reduction of the principles of thermodynamics, placing it in the context of the science of his time. The second is to present some of his work in 1890 on the foundations of statistical mechanics. He became interested first in thermodynamics and its relation with mechanics, drawing on the work of Helmholtz on monocyclic systems. After a period of skepticism concerning the kinetic theory, he read some of Maxwell's memories and contributed to the foundations of statistical mechanics. I also show that Poincaré's contributions to the foundations of statistical mechanics are closely linked to his work in celestial mechanics and its interest in probability theory and its role in physics.

## Introduction

The scientific oeuvre of Poincaré is immense, even if we consider only the fields of mechanics, astronomy, and mathematical physics. His interest in the theories of elasticity, waves, electromagnetism, and thermodynamics, as well, is marked by significant contributions. One of his contemporaries noted that he was more a conquerer than colonizer: he contributed significantly to many areas without staying there too long. Many of his memoirs and articles have an unfinished and open character. These general characteristics apply to his contributions to statistical mechanics.<sup>1</sup>

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<sup>1</sup>“A contemporary said of him, he was a conqueror, not a colonialist.” Boyer et Merzbach 1968, 676, §27. 3.

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The primary aim of this paper is to show the evolution of Poincaré's views on the mechanistic reduction of the principles of thermodynamics, placing it in the context of the science of his time. The second is to present some of his work, around 1890, on the foundations of statistical mechanics. He looked first to thermodynamics and its relationship with mechanics, inspired by Helmholtz's on monocyclic systems. After a period of skepticism about the kinetic theory, he carefully read some of the memoirs of Maxwell and contributed to the foundations of statistical mechanics. I also show that Poincaré's contributions to the foundations of statistical mechanics depend closely on his work in celestial mechanics and his interest in probabilities and their role in physics.

Classical statistical mechanics treats systems of material bodies subject to the laws of mechanics and with a huge number of degrees of freedom. It allows to one infer observable properties of these systems using statistical methods. Its initial domain was quite limited, to the case of gases. The kinetic theory of gases, for simplicity, had three formulations: the elementary kinetic theory of Clausius (1857–58), based on the concept of mean free path; Maxwell's second theory, which leads to the Boltzmann equation (1866); and the ensembles approach of Maxwell-Boltzmann-Gibbs (1879). Maxwell and Boltzmann, from specific models (elastic spheres, material points interacting through a Newtonian potential), then took the path of greatest generality to justify the equilibrium distribution, equipartition and the tendency towards equilibrium. This path is based on the formulation of Hamilton's mechanics, and it involves Liouville's theorem and the ergodic hypothesis. Josiah Willard Gibbs' 1902 book, *Elementary principles of statistical mechanics*, presented these methods in a systematic and independent way, compared to the initial context where ideas have emerged – that of the kinetic theory of gases. Twentieth-century statistical mechanics would be applied to more general systems, and its development would be closely linked to the history of quantum theory.

The kinetic theory of gases was struggling to establish itself at least until the end of the nineteenth century, except in the United Kingdom. The specific heat anomaly, and the small number of specific predictions, could be invoked against it. Its main achievement was a theory of transport phenomena, an area where it provided new relationships with, and access to, molecular parameters. Given the structuring role generally given to mechanics, the mechanical reduction of thermal phenomena could not fail to win favor; but further reductions existed which did not presuppose any specific model for substance and that did not make use of probabilities. The thermodynamics of the principles, a macroscopic theory, had a much more extensive domain than the field of kinetic theory. The analytical theory of heat, concerning heat diffusion, was able to develop without any connection to the kinetic theory.

## Strictly Mechanistic Reduction of Thermodynamics

Up to 1870, French scientists, despite their interest in the work of Clausius, showed very little interest in kinetic theory. The reception of the first kinetic theory of gases became a conceptual framework dominated by the tradition of laplacian molecular physics, and the optical tradition, originated by Fresnel and Cauchy. These two traditions share a molecular ontology, where everything is explained by postulating the existence of atoms or molecules centres of force. Concerning the nature of heat, vibration theory, proposed by Ampère (1835), allowed for a qualitative unity of light and heat, in the context of the Laplacian ontology. Ampère wrote: “it is to molecular vibrations and their propagation in their environment that I attribute all phenomena of sound; it is to atomic vibrations and their propagation in the ether that I attribute all those of heat and light.” These traditions bore many fruits in the fields of elasticity, hydrodynamics, elastic ether theory, etc. They enabled a unifying vision, ensuring consistency between the various theories, with celestial mechanics playing the role of an archetype; they benefited from the intellectual authority of masters such as Newton, Laplace, Fresnel, Ampère, etc.; and they were institutionally strengthened by the centralized and hierarchical character of the scientific community. These traditions coexisted with a more recent attitude of theoretical agnosticism, in experimental and theoretic work of Victor Regnault, who, however, still did not deny the molecular ontology. The identity of French physics also depended on a somewhat vague ideal of rigour and clarity in research and in the presentation of the results. Around 1885, Ampère’s version of the molecular physics program was still alive. It still promised a unifying vision. (Ampère 1835, 436, 434–435; Príncipe 2008, “Conclusions.”)

After 1850, molecular physics in the style of Laplace or Ampère found itself in competition with other approaches, especially outside France: (phenomenological) thermodynamics and kinetic theories. The latter involved only a minority of scientists around the world, because they had very few applications, many anomalies, and they involved ways new and difficult reasoning, especially in the second theory of Maxwell. Also, it should be noted that in the second half of the nineteenth century, there had been several kinetic conceptions of heat, and that someone like Clausius could accept or at least recognize this pluralism. This situation can be compared to that of the multiplicity of contemporary mechanical theories of the optical ether. The French, strong on Regnault’s work on static properties of gases and vapours, were particularly sensitive to the anomalies of the kinetic theories. They were working especially in the tradition of Ampère’s vibrational conception of heat. It was only after 1890 that the French took the kinetic theory as an object of scientific research, a change due to the intervention of scientists of a younger generation, more open to foreign physics. Henri Poincaré and Marcel Brillouin, both born in 1854, took an interest in Maxwell’s second theory and the foundations of statistical mechanics, in a way shaped by their own research programs.<sup>2</sup>

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<sup>2</sup>On the survival of several kinetic conceptions of heat, see Príncipe 2008, 8, and Chaps. 4 and 6.

In 1886 Poincaré obtained the chair of mathematical physics and probability calculus at the Sorbonne, which favored even more his interests in theoretical physics. He taught the mathematical theory of light, and in the spring of 1888, he taught a course on Maxwell's *Treatise on Electricity and Magnetism*. In the following years, he taught the electrical theories of Helmholtz, Hertz, Larmor and Lorentz. In 1888–89, he taught thermodynamics. He considered the question of compatibility between mechanism and thermodynamics, by analyzing the mechanical analogies proposed by Hermann von Helmholtz between the second principle and monocyclic systems described in the Hamiltonian formalism.

One should not confuse the mechanical analogies between the second principle and periodic or monocyclic mechanical systems, developed by Boltzmann, Clausius and Helmholtz, with concrete models of heat motion, in particular that of the kinetic theory. These analogies are formal analogies, and do not imply anything about the precise nature of the movement that is heat. These analogies were already of interest to the French scientists. Although around 1870, kinetic theory was taught in schools according to the views of Clausius, from the research point of view the French took a special interest in the analogy that Clausius proposed between the second principle and behavior of periodic systems. These analogies are compatible with vibration theory, the microscopic model for the material is not specified, and probabilistic considerations played no role.<sup>3</sup>

### *General Characteristics of Helmholtz's Approach*

In 1884, in “On the statics of monocyclic systems,” Helmholtz introduced the notions of polycyclic and monocyclic systems, presenting an analogy to the second principle for the case of reversible processes. In a memoir of 1886, “On the principle of least action,” he distinguished between complete and incomplete systems and considers irreversible processes. In this analogy the system obeys the conservation of energy, and is described by the Lagrangian equations that can be derived from the principle of least action. The use of this principle allows him to avoid assuming particular atomic models. This strategy originated in Maxwell's use of the Lagrangian method in his electromagnetic theory, to obtain the field equations without a detailed model of the ether; Poincaré considered this strategy to be Maxwell's great innovation (Poincaré 1890b, préface; see J. J. Thomson 1888, 4; Klein 1972, §5, 70–71; Bierhalter 1993, 442).

The last chapter of Poincaré's *Thermodynamique* is devoted to “The reduction of the principles of thermodynamics to the general principles of mechanics.” Here

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<sup>3</sup>Boltzmann was the first to develop these ideas; see Boltzmann 1866, Clausius 1871; Boltzmann 1871. A review of these articles may be found in Truesdell 1975, 59–60. On Clausius and the French, see Príncipe 2008, Chap. 7.

Poincaré expounds and criticizes the ideas of the German scientist.<sup>4</sup> Consider, following Helmholtz and Poincaré, a general mechanical system obeying Lagrange's equations (or, equivalently, Hamilton's equations). The system is described by a set of  $n$  generalized coordinates  $q$ ; the corresponding velocities are  $\dot{q} = dq/dt$ ; the state of the system is described by a single function, its Lagrangian:

$$L = L(q, \dot{q}) = T - V,$$

where  $T(q, \dot{q})$  is the kinetic energy of the system,  $V(q)$  the potential of the internal forces. Let  $P$  be the generalized external force corresponding to the generalized coordinate of the same index, and  $p = \partial L / \partial \dot{q}$  the generalized quantity of motion; then for each generalized coordinate we write the respective Lagrangian (Poincaré 1892a, §311):

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = P.$$

The dynamical evolution is governed by the system of these  $n$  equations.

Helmholtz distinguishes two groups of generalized coordinates: those which vary very slowly, the  $q_a$ , and those that vary rapidly, the  $q_b$ . The parameters that vary slowly are controlled by a macroscopic observer (for example volume, or the center of gravity of a body). A suggestive terminology was proposed by J. J. Thomson: he distinguished between macroscopically controllable variables  $q_a$  and the non-controllables  $q_b$ , corresponding to molecular motions, defining the thermal state of a body. When these rapid periodic motions are described by several non-controllable generalized coordinates  $q_b$ , Helmholtz speaks of polycyclic systems. In a monocyclic system, we admit the existence of certain relations between the velocities of the different parts of the system in such a way that these periodic motions are described by a single coordinate; those rapid motions that take place without altering the configuration of the system are analogous to the rotation of a flywheel or of a fluid circulating in a vortex (J. J. Thomson 1888, Chap. VI, "Temperature," §46; see Poincaré 1892a, §314; Langevin 1913, 706).

### ***The Analogue of the Second Principle for Reversible Processes***

Helmholtz mechanically defined a function sharing the same properties as entropy and the role of the temperature is played by the *vis viva* of these rapid movements. For the case of reversible processes that are infinitely slow, Helmholtz formulated

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<sup>4</sup>Darrigol described the method usually employed by Poincaré: "He read scientific texts quickly as a whole, and reconstructed the reasonings in his own manner. The result was often clearer than the original, revealed some essential features in full light, but overlooked other important ones", Darrigol 2000, 353.

three “natural” hypotheses. First, the velocities of the non-controllable coordinates are much greater than those of the controllable coordinates:  $\dot{q}_b \gg \dot{q}_a \approx 0$  (*hypothesis I*). The non-controllable coordinates are cyclic (or gyrostatic) – (*hypothesis II*). Therefore, they do not figure in the Lagrangian, and the corresponding equations are<sup>5</sup>:

$$P_b = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_b} \right) = \frac{dp_b}{dt}.$$

If  $dQ$  is the energy transmitted during the change of coordinates  $q_b$ , we have:

$$dQ = \sum P_b dq_b = \sum P_b \dot{q}_b dt = \sum \dot{q}_b \frac{dp_b}{dt} dt = \sum \dot{q}_b dp_b.$$

The kinetic energy is a homogeneous and quadratic function of the generalized velocities (if the connections don't depend explicitly on the time). Since the terms containing the  $\dot{q}_a$  are infinitely smaller, we have:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_a} \right) \approx \sum_b \alpha_{ab} \ddot{q}_b.$$

Admitting that the non-controllable coordinates have very small accelerations (since we are considering an equilibrium situation, and the constant temperature will be represented by the kinetic energy corresponding to an observably constant molecular velocity<sup>6</sup>) –*hypothesis III*, the anterior derivative is zero and the Lagrangian becomes:

$$\frac{\partial L}{\partial q_a} = -P_a \text{ (Poincaré 1892a, §316).}$$

By the previous considerations and by the theorem of homogeneous functions of degree  $n$ :

$$2T = \sum \dot{q} \frac{\partial T}{\partial \dot{q}} = \sum \dot{q} p \approx 2T_b = \sum \dot{q}_b p_b.$$

For the case of a monocyclic system, containing a single gyrostatic coordinate, we have (Poincaré 1892a, §317; Helmholtz 1884a, §3: “Monocyklische Systeme”):

$$dQ = \dot{q}_b dp_b, \quad 2T_b = \dot{q}_b p_b.$$

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<sup>5</sup>The hypothesis that the non-controllable variables do not figure in the potential energy is, from a modern point of view, reasonable for ideal gases but not for real gases, liquids and solids, where the interactions between molecules can't be ignored.

<sup>6</sup>Bierhalter maintains that Helmholtz was inspired by the first kinetic theories, for which the velocities of gas molecules were equal and constant. (Bierhalter 1993, 434 and 443.)

We can thus find an integrating factor of  $dQ$  for this case:

$$\frac{dQ}{\dot{q}_b} = dp_b \text{ and so } \frac{dQ}{T_b} = 2d(\log p_b).$$

We thus have an analogue to the second law of thermodynamics (for reversible processes) if we allow that the temperature corresponds to the kinetic energy. This is suggested by the kinetic theory of gases, as Helmholtz had remarked in his first article.<sup>7</sup>

Poincaré then analyzed the case of thermal equilibrium between two bodies. The coupling (called “isomore”, after the Greek expression for “same denominator”) between two monocyclic systems with the same integrating factor (temperature) corresponds to the condition of thermal equilibrium. Since in a monocyclic system, it is impossible to operate directly on the gyrostatic coordinates  $q_b$  by means of external forces, heat cannot be transmitted across these coordinates except by its coupling to another monocyclic system, and the coupling has to be isomore. Poincaré did not see how this theory would explain the fact that two bodies in contact, with the same temperature would not exchange calorific energy:

It is necessary to explain why, when two bodies with the same temperature are placed in contact, no heat passes from one to the other. The explanation has been attempted. The two bodies have been compared to two pullies with equal rotational velocities; when the pullies are turned, there is no shock and no transmission of living force from one to the other; when the two bodies are placed in contact, there will be no shocks between the molecules, the latter having the same velocity since the temperatures of the two bodies are the same. This explanation is far from satisfying.

By this, perhaps Poincaré means that the explanation is not compatible with the equipartition of energy: if two gases at the same temperature have molecules with different masses, their velocities should be different.<sup>8</sup>

### ***Vibratory Motion and Monocyclic Systems***

Poincaré asserts: “Molecular motions appear to be vibratory motions this way and that around a fixed point.” He does not say that this is restricted to solid bodies. He is probably referring to the vibratory theory of heat. Poincaré wants to show that in this case the kinetic energy is still an integral divisor of  $dQ$ , which represents

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<sup>7</sup>“Hier tritt die Analogie mit der kinetischen Gastheorie schon sehr deutlich heraus. Die Temperatur  $\theta$  ist der lebendigen Kraft proportional” (Helmholtz 1884a, fin du §3.) Martin Klein notes that Helmholtz had recognized that thermal motion is not strictly monocyclic: “I have affirmed from the beginning that thermal movement is not strictly monocyclic.” translated from Helmholtz 1884a, 757; see Klein 1972, 67.

<sup>8</sup>Poincaré 1892a, §331. See Bryan 1891, §26 et §27, Helmholtz 1884b, end of §6 “Koppelung je zweier Systeme”; Bierhalter 1993, 446. The name for the coupling is first explained at the beginning of §5 of Helmholtz 1884a.

an original contribution (Poincaré 1892a, §322–326; quote from the beginning of §322; see also §315).

Allow that there is only one parameter that varies rapidly. It is not cyclic, since it figures in the potential energy of a vibratory motion. Here hypotheses I and III remain valid, but not hypothesis II. The potential and kinetic energies are:

$$V = \frac{A(q_a) q_b^2}{2} + C(q_a), \quad T = \frac{B(q_a) \dot{q}_b^2}{2}.$$

The Lagrangian corresponding to this coordinate  $q_b$  is:

$$\frac{d(B\dot{q}_b)}{dt} + Aq_b = -P.$$

For a stationary vibratory motion  $P$  is zero and  $A$  and  $B$  are constant; in that case:

$$A = \omega^2 B, \quad q_b = h \sin(\omega t + \varphi), \quad \dot{q}_b = h\omega \cos(\omega t + \varphi).$$

Given the extreme rapidity of the oscillations, if one considers a sufficiently long time, it is the mean value of the kinetic energy that intervenes. As  $\overline{\cos^2 x} = 1/2$ , we have:

$$T = \frac{Bh^2\omega^2}{4} = \frac{Ah^2}{4}.$$

We can calculate the work of the force  $P$  during “a time  $\delta t$ , very small in an absolute sense but nonetheless very large in relation to the period of vibration”:

$$\delta Q = -\int P dq_b = \int \frac{dB}{dt} \dot{q}_b dq_b + \int B \frac{d\dot{q}_b}{dt} dq_b + \int Aq_b dq_b.$$

The first factor in the first integral of the second member may be considered as constant, the derivative  $dB/dt$  being small; the integral of  $\int \dot{q}_b dq_b$  taken over a time  $\delta t$  is replaced by the product of  $\delta t$  with the average value  $h^2\omega^2/2$  of  $\dot{q}_b^2$ ; thus the first integral of the second member becomes:

$$\frac{dB}{dt} \delta t \frac{h^2\omega^2}{2} = h^2\omega^2 \delta B$$

To calculate the two other integrals, Poincaré develops  $A$  and  $B$  by reference to increasing powers of  $t$ . The fact that  $\delta t$  is small permits one to consider only the linear part of these linear developments; the first derivatives of  $A$  and  $B$  are considered as constants. Moreover, one can choose  $\delta t$  in such a way that at the beginning and at the end of this interval  $q$  is null. After some clever calculations, Poincaré arrives at the expression (Poincaré 1892a, §325):

$$\frac{\delta Q}{T} = 3 \frac{\delta B}{B} + 2 \frac{\delta(\omega^2 h^2)}{\omega^2 h^2} - \frac{\delta A}{A},$$



which is an exact differential. Then, Helmholtz's theory permits the generalization of useful results for perfect gases to other states (of matter); in conclusion:

Clausius's theorem [for reversible processes,  $dQT$  is an exact differential] is, in consequence, well enough proven for the case of a vibratory state of molecules in the case of a swirling state (Poincaré 1892a, end of §325)

### *Irreversibility and Mechanism*

For a holonomic mechanical system, the kinetic energy is a quadratic function of the generalized velocities  $\dot{q}$ . To make the system return to its initial state by the same path, we can change the sign of the time parameter (change  $dt$  to  $-dt$ ); then the  $\dot{q}$  become  $-\dot{q}$  but the quadratic terms do not change, nor does  $V = V(q)$ ; thus the Lagrangian function remains the same. The same considerations apply to the Lagrangian equations  $\frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = P$ , since  $dt$  and  $\dot{q}$  simultaneously change sign while  $q$  and  $P$  remain indifferent. Therefore, Poincaré writes: "the system, when it reverts to its initial state, passes again exactly through those states that it had assumed in departing from the initial state; the transformations are therefore reversible" (Poincaré 1892a, §326).

However, Helmholtz found systems, called incomplete systems, for which the kinetic energy contains powers of odd exponents. He also showed that all the general equations that are valid for complete systems retain their form for the case of incomplete systems. In particular, the kinetic energy is an integral divisor of the quantity of heat for incomplete monocyclic systems. But if for complete systems,  $T = T(q_a, \dot{q})$  is a quadratic function of the generalized velocities, in the case of incomplete systems  $T'$  can have terms of odd degree with respect to the generalized velocities, because one part of the  $q_a = q_c$ , depends on the  $\dot{q}_b$ . The consequence is that a change of sign of the time implies a change in the Lagrangian – "irreversible phenomena could thus take place with incomplete systems; this is what Helmholtz admits." The analogy for irreversibility consists in comparing the thermal motion of molecules with hidden stationary movements. In the case of the spinning top, the top that spins is distinguished from the dead top by its capacity to resist the action of external forces that tend to change the direction of the action of rotation. Helmholtz conceives of this top as enclosed in a shell, thus remaining invisible and inviolable by humans.<sup>9</sup>

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<sup>9</sup>Poincaré 1892a, 442. An illustration of a case where the living force ceases to be proportional to the square of the velocity is that of a wheel turning on an axis equipped with a centrifugal force regulator; if the angular momentum increases, the bearings of the regulator recede from the axis while increasing the moment of inertia, so that the kinetic energy is not simply proportional to the square of the angular velocity. Poincaré 1892a, 431.

In spite of the interest of Helmholtz's ideas, Poincaré, by a sufficiently general argument, shows that they cannot account for irreversible phenomena. In his note, "On the attempts at a mechanical explanation of the principles of thermodynamics," he poses the following question: "Can we, by representing the world as composed of atoms, explain why heat never passes from a cold body to a hot one?"<sup>10</sup>

Suppose a general mechanical system obeying the equations of Hamilton. The Hamiltonian is:

$$H(p, q) = \sum p_a \dot{q}_a - L,$$

summing over the variables  $p$  and  $q$ .

For the case where the system is shielded from all external action, the Hamiltonian equations are,  $P_a = 0$ :

$$\dot{q}_a = \frac{\partial H}{\partial p_a}, \quad \dot{p}_a = -\frac{\partial H}{\partial q_a}.$$

If natural processes simultaneously obey the equations of mechanics and Carnot's principle, there must exist a function  $S(q, p)$ , "that is constantly increasing and that we will call the entropy". Then we can prove:

$$\frac{dS}{dt} = \sum \left( \frac{\partial S}{\partial q} \frac{dq}{dt} + \frac{\partial S}{\partial p} \frac{dp}{dt} \right) = \sum \left( \frac{\partial S}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial S}{\partial p} \frac{\partial H}{\partial q} \right) > 0.$$

Or, again, using the Poisson brackets,

$$\frac{dS}{dt} = \{S, H\} > 0.$$

Poincaré thought that he could demonstrate the impossibility of such an inequality while admitting that "the system, while remaining soustrait of all external action, is subject to such connections that the entropy is susceptible of a maximum". This state should correspond to a state of equilibrium. We can develop  $H$  and  $S$  in a power series  $(q_\alpha - q_\alpha^o), (p_\alpha - p_\alpha^o)$ , where the index  $o$  refers to the situation of equilibrium. The first term of the expansion can be cancelled owing to the fact that the two functions,  $H$  and  $S$ , are defined up to a constant. Since we assume the expansion is done close to the values corresponding to a maximum of entropy, the first derivatives cancel for  $q_\alpha^o, p_\alpha^o$ . If we consider small variations around the equilibrium configuration, we can restrict ourselves to the quadratic terms. The entropy will then be represented by a quadratic form (where the  $x$  represent either the  $q$  or the  $p$  and the derivatives are calculated from their equilibrium values):

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<sup>10</sup>Poincaré 1889, 550. Helmholtz's papers are explicitly cited at the beginning of this note. The proof appears also in Poincaré 1892a, §328 ff.

$$S = \sum_{i,j} \frac{\partial^2 S}{\partial x_i \partial x_j} (x_i - x_i^0) (x_j - x_j^0).$$

Since we admit that  $S$  has a maximum for  $q_\alpha^0, p_\alpha^0$ , this form is negative definite.

In order that the Hamiltonian can also be represented by a quadratic form, the first-order terms of its development should cancel. Poincaré justifies this as follows: “The derivatives of  $H$  cancel each other equally, because this maximum is an equilibrium position and so  $\dot{p}_\alpha$  and  $\dot{q}_\alpha$  must cancel.” The form  $H$  can be definite or indefinite. Poincaré tells us nothing about the relation between these conditions and those that can represent thermodynamic equilibrium.

Admitting that  $S$  and  $H$  are representable by quadratic forms near the maximum entropy, Poincaré shows that their Poisson bracket is also a quadratic form that is not positive definite. This result is intuitive, in the sense that the Poisson bracket transforms the squared terms of the quadratic forms into rectangular forms (of indefinite sign). Note that if the development of the Hamiltonian in series carries linear terms, the plausibility increases of the impossibility of the inequality  $(S,H) > 0$  increases (Poincaré 1892a, §330).

Poincaré ends this note with the following conclusion:

We should conclude that the two principles of the increase of entropy and of least action (understood in the Hamiltonian sense) are irreconcilable. Thus if Mr. Helmholtz has shown, with admirable clarity, that the laws of reversible phenomena derive from dynamics, it seems probable that we will have to look elsewhere for an explanation of irreversible phenomena, and give up on the familiar hypotheses of rational mechanics from which one derives the equations of Lagrange and Hamilton. (Poincaré 1889, 553)

In 1891, this note provoked a severe critique from George Bryan, who insisted that the equilibrium conditions imposed by Poincaré implied that all parts of the system are at rest. Since the entropy of a monocyclic system is the logarithm of a moment, if the latter is zero then the entropy will be infinite, contrary to Poincaré’s supposition. This criticism seems correct. Bryan is doubtless also correct that the kinetic molecular interpretation of temperature is incompatible with Poincaré’s equilibrium conditions. Zermelo briefly mentioned Poincaré’s note as another attempt to show that irreversible processes cannot always be explained by Helmholtz’s theory. Finally, the note got the attention of Louis de Broglie, for whom “these attempts at an interpretation of the second law of thermodynamics that is mechanical, but not statistical, have only led to very fragmentary results that only apply to very special models.” (Bryan 1891, 106–107; de Broglie 1948, Chap. V: 119; Zermelo 1896; see Bierhalter 1993, 455 and Brush 1976, §14.7, note 4).

## Poincaré and Maxwell’s Kinetic Theory of Gases

Poincaré published two editions of his course on thermodynamics. The second, in 1908, differed little from the first, except insofar as Poincaré’s opinion on the kinetic theory was concerned. At the end of the preface to the first edition, Poincaré

repeated the conclusion of his 1889 note: “I end with the theory of monocyclic systems. I will only cite my conclusion: Mechanism is incompatible with Clausius’s theorem.” In an issue of *Nature* in 1892, there was a debate between Poincaré and P. G. Tait. Tait accused Poincaré of having forgotten the kinetic theory in his course of *Thermodynamique*. Poincaré responded that he “wanted to remain completely apart from molecular hypotheses,” and that he found the kinetic theory “not very satisfying”. In the following year Poincaré’s position regarding the kinetic theory would become rather more favorable.<sup>11</sup>

Poincaré began to take an interest in the kinetic theory of gases in the course of his lecture on the papers of Maxwell, which was probably connected with his interest in ionic theories of electromagnetism (notably that of Lorentz), as the development of theoretical microphysics favored atomistic theories of heat. In 1893, Poincaré carefully read Maxwell’s paper of 1866 and raised a correct objection to Maxwell’s reasoning to justify the law of adiabatic expansion of a gas. This interesting criticism went straight to the foundations of statistical mechanics. Poincaré would take an interest above all in the most abstract justifications for equilibrium distribution, equipartition, and the tendency to equilibrium. That is to say, he favored the ensemble approach of Hamiltonian mechanics and he quickly saw the connection with a theorem in the three-body problem.<sup>12</sup>

### *The Article “Le mécanisme et l’expérience”*

Poincaré spoke for the first time about the importance of his recurrence theorem for the attempts at a mechanistic reduction of Carnot’s principle in the article “Le mécanisme et l’expérience” (1893a), published in the inaugural issue of the *Revue de Métaphysique et de Morale*. Experience shows that in nature there are “a crowd of irreversible phenomena,” which appear to be difficult to reconcile with mechanistic reduction. Poincaré divided mechanists into two groups. One was the side of Helmholtz, who did not use statistical reasoning, and the other was the English. Speaking of Maxwell (whom he considered to be English), he wrote:

The apparent irreversibility of natural phenomena has to do with the fact that molecules are too small and too numerous for the coarseness of our senses . . . Maxwell introduces the fiction of a “demon” whose eyes are subtle enough to distinguish molecules, and whose hands are small enough and quick enough to grasp them. For such a demon . . . there would be no difficulty in making heat pass from a cold body to a hot one . . . The kinetic theory of gases is up to now the most serious attempt to reconcile mechanism with experience. (Poincaré 1893a, 536)

<sup>11</sup>Poincaré 1892b, 485. Boltzmann stated, at the end of the preface to the first part of his *Leçons* (1896a), that “no one wanted to give much space to my work. It was cited with respect by Kirchoff and by Poincaré just at the end of his *Thermodynamique*, but not used when the occasion presented itself.”

<sup>12</sup>Poincaré 1893b; see the reference to this criticism in Boltzmann 1896a, note à la formule (187), see also Príncipe 2008, §10.4.1. On Poincaré’s contributions to electromagnetism and the theory of electrons, see Darrigol 2000, Chap. 9, especially §9.3.3.

Poincaré here speaks of the thought experiment now known as “Maxwell’s demon.” In a letter to P. G. Tait in December 1867, reprinted in his *Theory of Heat* (1871), Maxwell considers a finite being capable of seeing individual molecules. Controlling a barrier that separates the two parts of a chamber full of gas, this being could provoke a flow of heat (without compensation, that is without consuming work) letting only the fastest-moving molecules pass in one direction and only the slowest in the other. Maxwell therefore admits that the validity of the second law is only statistical (Maxwell to Tait, 11 déc. 1867, see also Maxwell to Strutt, 6 December 1870, in Maxwell 1990, vol. 2, 328–334, 582–583). Poincaré adds that the kinetic theory is not incompatible with his recurrence theorem:

An easily established theorem teaches us that a finite world, subject only to the laws of mechanics, will always pass again through a state very close to its initial state. On the contrary, according to accepted experimental laws, (if we grant them an absolute validity, and if we wish to push their consequences to the fullest), the universe tends to a certain final state from which it will not be able to depart. In this final state . . . all bodies will be . . . at the same temperature . . . Has anyone remarked that the English kinetic theories can escape from this contradiction? The world, according to them, first tends toward a state where it would remain for a long time without any apparent change . . . but it would not maintain that state forever . . . it would remain there only for an enormously long time, even longer than the number of molecules is large. This state would therefore not be the definitive death of the universe, but a kind of sleep, from which it would awaken after millions of millions of centuries.

This theorem, and the status of mechanism, were discussed by Zermelo and Boltzmann in 1896. The latter asserted, like Poincaré that the recurrences, for the usual macroscopic systems, escape our experience (Poincaré 1893a, 536. See Brush 1976, §14.7, 632–640).

## ***The Recurrence Theorem***

The recurrence theorem appears in Poincaré’s paper, “Sur le problème des trois corps et les équations de la dynamique,” which received the Oscar II of Sweden Prize, January 21, 1899.

## **The Three-Body Problem**

The three-body problem is one of the most celebrated problems of mechanics: given three material points interacting according to the law of universal gravitation, freely moveable in space; to find their motions from given initial conditions. From 1750 to the end of the nineteenth century, several hundred articles were published on this subject. Poincaré’s paper went through two formulations (1889 et 1890), of which only the second was published. The notion of the stability of a system, initially defined by the confinement of the variables that define the system, was replaced in 1890 by that of Poisson: the movable point  $P$  (describing, for example, a planet),

should return after a sufficiently long time, if not to its initial position, then to an arbitrarily nearby point to the initial position (recurrence).<sup>13</sup>

Some periodic solutions were already known. Poincaré studied the non-periodic solutions (the asymptotic and the doubly asymptotic solutions) and developed qualitative methods. These non-periodic solutions are infinitely improbable, but “taken together with the periodic solutions . . . make up, so to speak, the tangled fabric formed by the totality of general orbits.”<sup>14</sup>

### The Concept of Integral Invariant

The concept of the integral invariant was created by Poincaré in the framework of his research on the differential equations of Hamiltonian systems. Recall his definition:

$$\frac{dx_1}{X_1} = \frac{dx_2}{X_2} = \dots = \frac{dx_n}{X_n} = dt,$$

a system of differential equations. Let  $x_1^0, \dots, x_n^0$  be any point in a domain  $D(0)$  of  $k$  dimensions. This set of points will occupy, at another instant  $t$ , another domain of  $k$  dimensions,  $D(t)$ . A  $k$ -dimensional integral over the domain  $D(t)$  is an integral invariant of order  $k$  of the system of equations if the value of this integral is independent of  $t$ . The typical example is the constant volume of a determinate part of an incompressible fluid. For a Hamiltonian system with  $n$  degrees of freedom, Poincaré shows that:

$$I_1 = \int \sum_i dq_i dp_i, I_2 = \int \sum_{i,k} dq_i dp_i dq_k dp_k, \dots, I_n = \int dq_1 dp_1 dq_2 dp_2 \dots dq_n dp_n,$$

are integral invariants. In particular, the integral  $I_n$  is an integral invariant corresponding to the condition of incompressibility of a fluid in the phase space (Liouville’s theorem).

Poincaré took great advantage of the invariants  $I_1, I_n$  in his researches on some special solutions (periodic solutions of the second type and doubly asymptotic solu-

<sup>13</sup>On the history of the problem, see Whittaker 1899 and Barrow-Green 1997. The first version, that of 1889, was printed but not published, because a crucial error was detected in the demonstration of stability. It was in the second version that the recurrence theorem played a decisive role in the structure of the paper. See Robadey 2006.

<sup>14</sup>Von Zeipel 1921, in *Œuvres de Poincaré*, vol. 11, 308. Here is an example of an asymptotic orbit, in a system consisting of a Sun, an Earth, and two moons of infinitely small mass: “Suppose an observer placed on the Earth and slowly turning on himself so as to be in constant view of the Sun. The Sun will appear to him to be at rest, and the moon L1, with a periodic orbit, will appear to describe a closed curve C. Moon L2 will then describe for him a sort of spiral of which the arms, more and more tightly wound, will indefinitely approach the curve C.” Poincaré 1891, *Œuvres* vol. 8, 532–533.

tions) and on the question of the stability of motion. He immediately remarked on the existence of unstable orbits: “The existence of asymptotic solutions . . . suffices to show that if the initial position of point P is suitably chosen, the point P will not re-pass an infinite number of times as nearly as one might like to the initial position”. Poincaré went on to establish the exceptional character of these unstable solutions: “There will be an infinity of solutions of the problem that will not have stability . . . in the sense of Poisson; but there will be an infinity that do have it. I would add that the first can be regarded as exceptional” (Poincaré 1890a Sect. 8, “Usage des invariants intégraux”, *Œuvres* vol. 7, 313–314).

Poincaré began by demonstrating the following theorem. Consider a space of  $N$  dimensions and assume that the hypervolume  $\int dx_1 dx_2 \dots dx_N$  is an integral invariant; if the point P remains at a finite distance and if we consider any region  $g_0$  of this space, no matter how small the region  $s$ , there will be trajectories that cross it an infinite number of times. The demonstration shows that the total volume of the series of regions of space that succeed the region  $g_0$  becomes infinite if there is no recurrence (Poincaré 1890a, *Œuvres* vol. 7, 316). The calculation of the time of return is a very delicate problem on which Poincaré, as far as I know, said nothing in his papers.

### The Exceptional Character of Trajectories Without Recurrence

After his study of asymptotic solutions, Poincaré studied possible trajectories without the property of recurrence. The previous demonstration did not seem to allow for this type of trajectory, and it seemed necessary to harmonize the two results. The quasi-periodic character is almost always there in the evolution of a conservative system; Poincaré expressed it using the concept of probability. This concept appears explicitly in the enunciation of the corollary of the recurrence theorem in the final version of the paper (1890a):

Corollary. It follows from the preceding that there exists an infinity of trajectories that cross the region  $\delta(P_0)$  infinitely many times; . . . but there may exist others that only cross the region a finite number of times . . . . It will suit our purposes to say that the probability that the initial position of a mobile point P belongs to a certain region  $\delta(P_0)$  is to the probability that the initial position belongs to another region  $\delta'(P_0)$  as the volume of  $\delta(P_0)$  is to the volume of  $\delta'(P_0)$ .

The probabilities being thus defined, I propose to establish that the probability that a trajectory  $\delta(P_0)$  starting from a point does not cross this region more than  $k$  time is zero, no matter how large  $k$  is or how small the region  $\delta(P_0)$ . That is what I mean when I say that trajectories that only cross  $\delta(P_0)$  a finite number of times are exceptional. (Poincaré 1890a, *Œuvres* VII, p. 316)

The historian Anne Robadey remarks that the recurrence theorem (and its corollary), of which the proof is non-constructive, represents, in the history of mathematical theorems, one of the first examples in which a property is shown to be valid for “almost all” of the objects in a given class. Poincaré directly connected the concept of probability and the relative measure of a region. Today

we characterize the exceptional character of trajectories without recurrence by saying that they constitute a set of measure zero. The measure theory developed by Borel, Lebesgue, and others came after this paper of Poincaré's. The development of ergodic theory is intimately connected to these developments. The influence of Borel on Lebesgue, and the influence of Poincaré on the latter, has already been remarked on. George Birkhoff, one of the mathematicians who contributed the most to the theory of ergodicity, at a conference on "Probability and physical systems" (1931), considering the problem of exceptional trajectories (and its lack of physical significance in light of the impossibility of rigorously determining the initial conditions), eulogized Poincaré as the first to use, in an intuitive manner, considerations "of probability 1"; that is, the first to consider, in problems of theoretical mechanics, sets of measure zero (Von Plato 1994, 110; Poincaré 1896).

### ***"On the Kinetic Theory of Gases" (1894)***

In 1894, Poincaré wrote an article presenting his lecture on the foundations of statistical mechanics and analyzed Kelvin's criticism of the validity of the ergodic hypothesis (1892). This criticism immediately aroused the interest of several British scientists (Watson, Burbury, Bryan and Rayleigh) as well as that of Boltzmann. Poincaré showed that Kelvin's examples were not genuine counter-examples to equipartition.<sup>15</sup>

Poincaré recognized that great efforts had been expended to develop the kinetic theory, and that the results of those efforts had not been proportional to the effort expended; he stated:

I doubt that, up to the present time, it can account for all the known facts. But it's not a question of knowing whether it is *true*; that word, where such a theory is concerned, *has no meaning*; it is a question of knowing whether its fertility is spent, or whether it can still help with further discoveries. (Poincaré 1894, 246)

By that, Poincaré wanted to indicate that the kinetic theory has the status of an analogy, a scientific illustration in the sense of Maxwell (see Príncipe 2010, 2012).

After recalling the basic conception of the kinetic theory, already presented by the Bernoullis, Poincaré emphasized that "the theory only took on its definitive form when Clausius proved his virial theorem." The internal virial allows us to understand how remote the behavior of real gases can be from that of an ideal gas. Then he mentions Clausius's hypothesis of the proportionality of the energies associated with the components of molecules to the kinetic energy of translation. This postulate of Clausius is justified by the theorem of equipartition, of which

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<sup>15</sup>See Thomson 1892 and Brush 1976, §10.9, who concludes: "The outcome seemed to be a general agreement that most of Kelvin's test-cases did not prove any violation of the equipartition theorem, but, on the other hand, that one could not be sure that the theorem was always valid in systems of a finite number of particles". See also Príncipe 2008, §10.4.2.



one possible foundation is the ergodic hypothesis. Recall first the genealogy of that hypothesis, which came to Poincaré from reading Maxwell's 1879 paper, "On Boltzmann's Theorem on the average distribution of energy in a system of material points," in which Maxwell took up the global approach introduced by Boltzmann. In 1868, Ludwig Boltzmann criticized Maxwell's proof of the stability of the distribution with respect to binary collisions, and introduced the distribution that Gibbs would call micro-canonical. In the case of a gas subject to the action of an external force field, he introduced the global distribution, a function of the positions and the velocities of the  $N$  molecules of a gas:

$$\rho(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{V}_1, \vec{V}_2, \dots, \vec{V}_N),$$

$\rho d\sigma$  giving the fraction of the time (considering a very long time) that the system spends in the element  $d\sigma = d^3r_1 d^3r_2 \dots d^3r_N d^3V_1 d^3V_2 \dots d^3V_N$ . He first shows that if a system is contained at an instant  $t$  within a volume element  $d\sigma$  of the phase space, then at a later instant  $t + \delta t$  it will be contained in a volume element  $d\sigma'$  with the same volume ( $d\sigma = d\sigma'$ , Liouville's theorem). He deduces from this that the density  $\rho$  is constant along the entire trajectory. Finally, he admits that the trajectory of the system in this  $6N$  dimensional space fills the energy level  $E = \text{cte}$ . It then results that the density  $\rho$  is uniform on this level. Starting from this distribution, characterizing a large isolated system, Boltzmann arrived at the characteristic distribution of a small subsystem (one molecule, for example) that is weakly coupled (thermally coupled) with its complement (the remainder of the large system, which plays the role of thermostat). If  $E^*$  is the energy of this subsystem, then the distribution associated with it is  $\alpha e^{-2hE^*}$ . The equipartition of the energy for the quadratic degrees of freedom is a consequence of this distribution. This law, now known as the Maxwell-Boltzmann distribution or the canonical Gibbs law, still remains an essential element of statistical mechanics.<sup>16</sup>

In 1879, Maxwell attributed to Boltzmann "the general solution of the problem of the equilibrium of kinetic energy among a finite number of material points," and noted that "The only assumption which is necessary for the direct proof [of the equipartition theorem] 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".<sup>17</sup>

In 1894, Poincaré noted that the mean value of a dynamical magnitude should, if it is accessible to observation, be comprised of "the mean taken at once with respect to time and with respect to the various molecules; it is, so to speak, a mean value of mean values." This assertion suggests that for him, the equivalence of the two

<sup>16</sup>Boltzmann 1868. A partial translation appears in Barberousse 2002, 150–165. See Darrigol and Renn 2000.

<sup>17</sup>Maxwell 1879, *Scientific Papers*, 714. Maxwell recognized that one could imagine systems where this condition (the ergodic hypothesis) is a false, but he admits that, for a gas enclosed in a container, the interaction of the molecules with the barrier permits an explanation of its validity. *ibid.*, 714–715.

means was not evident (Poincaré 1894, 249). Poincaré gives the following form to the equipartition theorem:

If there is no other uniform integral than that of the living forces, and if the living force of the system is decomposable into two independent parts, the mean values of these two parts, over a very long time, will be among themselves as the number of their degrees of freedom.

Poincaré noted that the existence of other uniform integrals, for the case of a material system that is free in space (for which there is conservation of linear momentum and of angular momentum), changes this form (a case considered in the second part of Maxwell's 1879 paper). The modified form insists that the energy must be the only uniform integral (see below; Poincaré 1894, 253).

Poincaré recognized the anomaly of specific heats, but he believed that this difficulty, though unresolved, would perhaps not be insurmountable (Poincaré 1894, 255). The isotropic distribution of velocities for a gas at equilibrium, without action by an external force, is another consequence of "Maxwell's theorem." All "the preceding suffices to show the importance of Maxwell's theorem [the equiprobability of domains of equal volume in the available phase space of a system]; this is the veritable cornerstone of the theory of gases, which would be lost without it." Poincaré gave a form of "Maxwell's postulate," allowing him to justify "Maxwell's theorem," which corresponds not to the ergodic hypothesis, but to the quasi-ergodic hypothesis:

Maxwell admits that, whatever the initial situation of the system, it will always pass an infinite number of times, I don't say through all the situations compatible with the existence of integrals, but as close as one would like to any one of these situations.<sup>18</sup>

This expression was surely inspired by his recurrence theorem, in which return is not exact.<sup>19</sup>

### *A Theorem on Non-uniform Integrals*

Liouville's theorem implies that the motion of a representative point defines a continuous point transformation that conserves the extension in phase. In the ensemble approach this implies that the distribution function corresponding to the

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<sup>18</sup>Poincaré 1894, 252, 255–256. Equiprobability is considered in Poincaré 1896, §89 (course on probability of 1893–94). There he considers a conservative mechanical system obeying Hamilton's equations, for which the initial conditions are unknown; he admits that the probability of finding it within a volume is proportional to the magnitude of the volume, and deduces Liouville's theorem.

<sup>19</sup>Brush 1976, 372, believes that Poincaré confused the two hypotheses. It would be more natural not to assume that Poincaré was unaware of the distinction between the two hypotheses, but that he found the second one more natural. Maxwell did not distinguish them. Maxwell 1879, *Scientific Papers* 2, 720. In rebuttal, von Plato 1994, 102, praises the 1894 article: "[It] contains the essential concepts that much later became the tools of the trade of ergodic theory: the requirement that the trajectories be dense, and that this holds, except for a set of initial conditions of probability 0".

permanent state should be constant along each trajectory. Therefore the equilibrium distribution should, in all generality, have the form

$$\rho_0(q, p) = F(E, \psi_2, \dots, \psi_{2n-1}),$$

$F$  being an arbitrary function of the integrals  $\psi_i$  (functions of  $p$  and of the  $q$  that remain constant along the length of each trajectory) of the system of  $2n$  Hamiltonian equations for a conservative system. Maxwell, in 1879, believed that it is the ergodic hypothesis that justifies that the function  $F$  depends only on the energy. Boltzmann reflected a great deal on the justification of the ergodic hypothesis and therefore on the “effacement” of the  $2n-2$  first integrals, and it is probable that these reflections made him doubt the validity of that hypothesis for the general case of gases composed of polyatomic molecules.<sup>20</sup>

Toward 1890, Poincaré formulated a theorem asserting the non-uniformity of the integrals, apart from energy, of the canonical equations of celestial mechanics. This result concerned perturbative methods of solving Hamilton’s equations. The theorem illuminated one of the major problems in the foundations of classical celestial mechanics – the justification of the role of energy in the distribution function. A difficult and often ignored question arises. Chapter V of the first volume of the *Nouvelles méthodes de la Mécanique céleste* (1892c) is dedicated to the non-existence of uniform integrals of the canonical equations. Consider a conservative mechanical system, described by  $2n$  parameters:  $n$  coordinates  $q$  and  $n$  conjugate momenta  $p$ . Poincaré admits that the mechanical system is stable in the sense that no particle leaves a limited region of space. The kinetic energy, the potential energy, and the total energy are easily defined. The  $2n$  canonical equations admit  $2n-1$  integrals that are independent of time. These integrals are in general non-uniform functions:

The canonical equations of celestial mechanics do not admit (excepting those exceptional cases that are discussed separately) uniform analytic integrals apart from the energy. (Poincaré 1892c, 8, 253. See also Born 1925, Brillouin 1964, 109)

A uniform integral of Hamilton’s equations is a function of the  $p$  and the  $q$  that remains constant in the course of the evolution of the system. According to the theorem, the energy is the only “well behaved” integral; the others are non-analytic functions, with discontinuities and “bizarre” behaviors. A non-uniform integral of the canonical equations can take a value infinitely close to a given value in the neighborhood of any point of the phase space.

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<sup>20</sup>Boltzmann early on doubted the validity of the ergodic hypothesis, which is why he preferred in 1871 to return to a generalization of Maxwell’s *Ansatz*. When he adopted ensembles, he preferred not to justify them by ergodicity, but rather by the empirical fact that the thermodynamic behavior of a system does not depend on initial conditions for given external thermodynamic conditions; see Gallavotti 1994, §3, Barberousse 2000, Chap. V, 158.

This result had already figured in the paper on the three-body problem (1889–90). There Poincaré considered the attempts to integrate the equations of celestial mechanics by trigonometric series whose convergence was unproven. He showed that the series introduced by Hugo Gylden and by Anders Lindstedt were divergent. This divergence followed from the above general result: the absence of a uniform analytic integral apart from the integral of the living forces that will be valid for all the equations of dynamics (see Robadey (2006, 22, 25–26, 31) and Barrow-Green (1997 § 5.9)).

Poincaré's proof supposes the existence of multiperiodic perturbative solutions by the method of Delauney (variables action-angle). He shows by *reductio* that if there exists another uniform integral besides the energy, the nullity of its Poisson bracket leads to impossible relations for its Fourier coefficients at various orders of perturbation. Note that the validity of Poincaré's theorem is doubted by some modern authors.<sup>21</sup>

Léon Brillouin notes that non-analyticity (non-uniformity) is closely connected with non-separability:

This condition [established by Poincaré's theorem] resulted in discontinuities in the solutions obtained by the Hamilton-Jacobi method. It may be explained by the following statement: For a given mechanical problem with energy conservation and no dissipation, one may find a few variables that can be separated away from the system. When this has been done, one is left with the hard core of non-separable variables. This is where the Poincaré theorem applies, and specifies that the total energy is the only expression represented by a well-behaved mathematical function. Many other quantities may appear as "constants" of a certain motion, but they cannot be expressed as analytical and uniform integrals. This means that any kind of modifications in the problem may provoke an abrupt and sudden change of the "constants". This discontinuity may be the result of a very small change in any parameter in the mechanical equations, or, also, in any small change in the initial conditions. (Brillouin 1964, 128)

For him, "The Poincaré theorem contains the justification of Boltzmann's statistical mechanics, which should apply when (and only when) the total energy remains the only well-behaved first integral". In effect, it is reasonable to admit that the forces between molecules and the interactions between partitions are perturbations removing all degeneracy in an action-angle development.<sup>22</sup>

Poincaré himself did nothing to make his theorem known to physicists. His discussion of the role of the principle of conservation of energy, in the preface to his *Thermodynamique* (1892a), does not mention this result. He mentions it

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<sup>21</sup>Kolmogorov in 1954 published a theorem contrary to Poincaré's. Arnold and Moser generalized Kolmogorov's result and formulated a theorem known by the acronym KAM. See: Arnold 1978; Cercignani 1998, 158.

<sup>22</sup>Brillouin 1964, 125–126. Borel was one of the rare authors who stated this theory in a treatise on statistical mechanics. Borel 1925, 20.

only in his 1894 article on the kinetic theory, saying only that energy is the only uniform integral for the kind of system for which Maxwell's postulate is reasonable (Poincaré 1894, 253).

## Conclusion

The scientific personality of Poincaré is characterized by the breadth of his interests, his familiarity with both French research traditions and foreign works, his predilection for the big questions, his critical spirit, and his subtlety. He took a profound interest in celestial mechanics, electrodynamics, thermodynamics, the calculus of probabilities, among many other questions. His creativity allowed him to build bridges between different domains of his research.

Poincaré was aware of the problem of the mechanistic reduction of Carnot's principle. First, he was interested above all in Helmholtz's work on monocyclic systems. The issue had already had an echo in France (Alfred Ledieu and Jules Moutier were interested in a similar analogy proposed by Clausius). Poincaré admired Helmholtz's work in other domains, which doubtless encouraged this more specific interest. Poincaré taught and developed these ideas, shortly after their publication; he extended Helmholtz's argument in the case of vibratory motions that represent heat in Ampère's conception. And he showed that, in spite of their interest, these considerations would not allow for an explanation of irreversibility. At that time, he knew only the outlines of the work of Maxwell and of Boltzmann on the kinetic theory. Electromagnetism was one of the subjects of his first courses on mathematical physics (1889/90); Poincaré gave particular emphasis to the epistemological significance of Maxwell's Lagrangian formulation of electromagnetism, which is one of the great examples of a new phase in the evolution of that physics that Poincaré called "the physics of the principles". In this framework, Maxwell formulated the theorem of the existence of an infinite number of mechanical models compatible with a Lagrangian system, which suggests an argument for the underdetermination of theories by empirical evidence. In addition, Maxwell's reflections anticipated Poincaré's idea of a plurality of inter-translatable languages. This was an idea that encouraged Poincaré's interest in all of Maxwell's work.<sup>23</sup>

Poincaré was able to establish connections between his research in celestial mechanics and the foundational problems of classical statistical mechanics (the ergodic hypothesis and irreversibility). In these two domains, he gave a central role to the concept of probability for continuous variables. He noted that if his recurrence theorem were incompatible with the absolute validity of the second principle, it would be compatible with the probabilistic interpretation of entropy. Another result obtained by Poincaré, the non-uniformity of the first integrals of Hamilton's

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<sup>23</sup>Príncipe 2012. Helmholtz was then a foreign member of the Académie des Sciences.

equations, also concerned the foundations of statistical mechanics. The importance of this result was not emphasized by Poincaré, and it remained in the shadows until the 1920's. It stays ignored by most treatments of statistical mechanics. He also touched on the problem of the limits of prediction in classical mechanics. In his so-called popular works, Poincaré affirmed his epistemological pluralism, and often spoke of the kinetic theory and the importance of probabilities.

In 1906, Poincaré would publish a paper on the kinetic theory of gases, in which he showed a profound understanding of Gibbs's treatise and gave a very subtle analysis of irreversibility. He introduced two concepts, *coarse-grained entropy* and *fine-grained entropy*, which represent a "substantialization" of the ideas discussed in Chap. XII of Gibbs's treatise: fine entropy always remains constant, while coarse entropy, that of the physicists, "that which depends on our usual means of investigation," is constantly increasing (Poincaré 1906, *Œuvres*, vol. 10, 591). The tendency to irreversibility is therefore a consequence of the limitations on our means of observation. Poincaré would treat two problems that were simpler than that of gases (the small planets, and a gas in one dimension) to show that the tendency to equilibrium can be treated analytically. He showed that, for a system with a finite number of particles, recurrences are inevitable and Carnot's principle is not absolutely valid. Poincaré also showed that, in a system that comes to equilibrium, its apparent disorder may hide a latent order because of previous state of equilibrium. This last notion is motivated by his reflections on the initial notions of Boltzmann's treatise, notions of disposition without molar organization – *molar ungeordnet* – and of disposition without molecular organization – *molekular ungeordnet*. The article ends with the difficult problem of rarified gases. Poincaré suggests that the behavior of gases can be composed as a mixture of the behavior of a gas in one dimension and the three-dimensional gas of the kinetic theory; for short times of evolution, the first kind of behavior is fundamental. (See Príncipe 2008, §10.8).

Poincaré's epistemological conceptions, his appreciation of the limits of classical mechanics, and his taste for the theory of probability explain his openness to probabilistic explanations in physics, an openness that was rather rare at this period in France. His writings on probability and on the kinetic theory inspired the next generation of researchers, especially Émile Borel.

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