The principle of identicality and the foundations of quantum theory.
I. The Gibbs paradox

Peter D. Pešić
St. John's College, Santa Fe, New Mexico 87501

(Received 4 February 1988; accepted for publication 3 April 1991)

The development of the concept of indistinguishability in the writings of Gibbs is traced, leading from the "Gibbs paradox" to his definition of generic phase.

I. INTRODUCTION

This is the first of two papers that reexamines the place of indistinguishability and identicality in the foundations of quantum theory. The principle of identicality is defined as the hypothesis that each fundamental class of physical states is composed of completely indistinguishable entities which can be characterized by certain exactly equal observable parameters (such as mass or charge). The question of identicality in the context of statistical mechanics with special attention to the so-called Gibbs paradox is considered. A close examination of Gibbs' writings shows the way in which Gibbs introduced a basic notion of identicality in his concept of generic phase. In the following paper, the further historical development of the question will be examined, especially in Planck's work.

II. GIBBS' EARLIER CONSIDERATION OF IDENTICAL GASES

The origins of the fundamental question of whether there can be identical entities in the world seem to lie in Greek thought.[1] The question already is considered by Aristotle and is significant for the early atomists. By the early 19th century Dalton had written that "the ultimate particles of all homogeneous bodies are perfectly alike."[2] Yet Boltzmann emphasized that the distinguishability and continuity of motion of each material point should be the "first fundamental assumption" of mechanics.[3] Since then, many writers have pointed to what is usually called the Gibbs paradox as a telling case in which considerations of identicality have important physical consequences. The unfolding of this matter in Gibbs' thought over a quarter of a century is not so well known. His sustained consideration of it reveals an essential problem important for quantum theory.

Gibbs first mentions this matter (which he never calls a "paradox") in his seminal paper of 1876, *On the Equilibrium of Heterogeneous Substances.*[4] He calculates the increase of entropy when two different gases, each initially occupying volume $V/2$ (at the same pressure p and temperature T) and separated by an impermeable membrane, are allowed to diffuse together into the whole volume V when the membrane is removed. The result is (pV/T) ln 2.[5] The question ensues if the two gases on either side of the membrane are now made to be *identical.* For then it is evident that the entropy must not change when the membrane is removed.

How does Gibbs react? It is noteworthy that this situation does not amount to a "paradox" for him since he goes on to note a sharp distinction between the cases of identical and nonidentical gases:

> When we say that when two different gases mix by diffusion, as we have supposed, the energy of the whole remains constant, and the entropy receives a certain increase, we mean that the gases could be separated and brought to the same volume and temperature which they had at first by means of certain changes in external bodies, for example, by the passage of a certain amount of heat from a warmer to a colder body. But when we say that when two gas-masses of the same kind are mixed under similar circumstances there is no change of energy or entropy, we do not mean that the gases which have been mixed can be separated without change to external bodies. On the contrary, the separation of the gases is entirely impossible. We call the energy and entropy of the gas-masses when mixed the same as when they were unmixed, because we do not recognize any difference in the substance of the two masses. So when gases of different kinds are mixed, if we ask what changes in external bodies are necessary to bring the system to its original state, we do not mean a state in which each particle shall occupy more or less exactly the same position as at some previous epoch, but only a state which shall be undistinguishable from the previous one in its sensible properties. It is to states of systems thus incompletely defined that the problems of thermodynamics relate.[6]

Thus it seems that the two cases "stand on a different footing" (in his words) and the sense of paradox is absent from his account. Yet the final sentences show Gibbs already considering what shall be the properties of the subsequent state of a system "undistinguishable ... in its sensible properties" from a prior state. This state will emerge much later as Gibbs' notion of generic phase.

Gibbs' further comments reveal the way in which the matter refuses to be dismissed from his mind:

> But if such considerations explain why the mixture of gas-masses of the same kind stands on a different footing from the mixture of gas-masses of different kinds, the fact is not less significant that the increase of entropy due to the mixture of gases of different kinds, in such a case as we have supposed, is independent of the nature of the gases.

That is, the difference between the two cases (the gases identical or not) which makes them seem quite dissimilar is outweighed in his mind by the way his expression for the change of entropy does not depend on the nature of the gases in *any* way. He goes on to speculate on the nature of the possibile dissimilarity between atoms in a way that will be very significant:

> Now we may without violence to the general laws of gases which are embodied in our equations suppose other gases to exist than such as actually do exist, and there does not appear to be any limit to the resemblance which there might be between two such kinds of gas.

Here, then, emerges the central question: Is it possible for atoms to differ in any amount whatever, perhaps even only infinitesimally, or is there a "limit" to such resemblance? We note that Gibbs himself seems to assume the first of these possibilities, that the properties of atoms are continuously variable. But it is most interesting that, in his mind too, the question has at least been broached (note his circumspect use of "appear"), even though here he has not yet departed from the classical conclusion. As he continues, the matter refuses to be settled simply:

> But the increase of entropy due to the mixing of given volumes of the gases at a given temperature and pressure would be independent of the degree of similarity or dissimilarity between them.

His further remarks show him thinking more and more probingly about the exact meaning of similiarity between atoms:

> We might also imagine the case of two gases which should be absolutely identical in all the properties (sensible and molecular) which come into play while they exist as gases either pure or mixed with each other, but which should differ in respect to the attractions between their atoms and the atoms of some other substances, and therefore in their tendency to combine with such substances.

Here Gibbs considers whether two atoms can be identical in themselves but differ in their interactions—i.e., whether the source might be separated from its field. This interesting conjecture is at variance with the view espoused by Maxwell and Faraday which subsumes the source completely in the field and which does not allow two identical sources to have variant fields.[7] This conjecture also raises the deepest concerns about whether identicality is essentially a characteristic of the material source in itself (apart from its interactions) or whether it also embraces all the interactive manifestations of the atom. One reads on with considerable curiosity to see in what light Gibbs will view his own suggestion:

> In the mixture of such gases by diffusion an increase of entropy would take place, although the process of mixture, dynamically considered, might be absolutely identical in its minutest details (even with respect to the precise path of each atom) with processes which might take place without any increase of entropy. In such respects entropy stands strongly contrasted with energy. Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have once been mixed. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.

First it seems that Gibbs indeed recognizes that identicality must extend to the interactions as well as to the sources, for in his hypothetical case he concedes that identical sources with variant fields will still lead to an increase in entropy and hence are essentially distinguishable in nature (also confirmed by the thought experiment of reseparating the constituent gas masses). The unspoken conclusion is that the distinguishability of atoms lies as much in their interactions as in the material characteristics of the central source, an observation that emphasizes the irreducible and fundamental aspects of identicality which will return in quantum theory.

Gibbs emphasizes the contrast between energy and entropy by way of showing how the question of distinguishability is really raised only in the context of entropy, which he considers an essentially statistical concept, and not in the context of energy, which has no regard to the distinctness of the atoms considered and is not inherently statistical. Here is a foreshadowing of the statistical character of quantum theory, especially in Planck's earliest formulations of the quantum hypothesis from considerations of entropy.

Finally, Gibbs notes that "there is perhaps no fact in the molecular theory of gases so well established as that the number of molecules in a given volume at a given temperature and pressure is the same for every kind of gas when in a state to which the laws of ideal gases apply." At this point, Gibbs passes from purely thermodynamic considerations to reiterate its bearing on the atomic theory of matter. If this theory is to apply to gases, then in interdiffusing gases "the increase of entropy is therefore determined by the number of these molecules [i.e., by pV/T] and is independent of their dynamical condition and of the degree of difference between them." Though it is not explicitly stated, Gibbs seems to be saying that there are only two possible cases for atomic matter: Either the atoms are exactly identical or they are not. The result he has obtained for the entropy of gases in these two cases indicates that there is a discontinuity between these two cases.

III. GIBBS' LATER CONSIDERATION OF IDENTICALITY

Gibbs next addresses this issue 25 years later in the final pages of his famous *Elementary Principles in Statistical Mechanics*.[8] By the date of 1901 attached to Gibbs' preface, we realize that this work is notably simultaneous with Planck's first statements on the quantum hypothesis. Indeed, as a biographer remarks, these pages of Gibbs are the "crowning achievement" of a work which itself was "a fitting capstone to Gibbs' scientific career."[9] Both the subtitle of the work and Gibbs' preface show his concern to give a "rational foundation" for thermodynamics, and they show the essential significance he attached to clarifying the nature of the concept of entropy. Following Newton's very words, Gibbs writes:

> Moveover, we avoid the gravest difficulties when, giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. In the present state of science, it seems hardly possible to frame a dynamical theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms. Yet any theory is obviously inadequate which does not take into account of all these phenomena.[10]

In this context, he mentions the then current difficulty concerning the degrees of freedom of a diatomic gas, which were expected, classically, to number six, but which, experimentally, seemed only to number five. It is striking that this very difficulty and the physical problems he has just enumerated are those that quantum theory will address.

In echoing Newton's phrase *hypotheses non fingo* Gibbs clarifies the importance of rectifying questions concerning entropy. For if we defer the difficult problem of the true nature of the fundamental forces, we are left facing the immediate problem of making rational the macroscopic quantities (such as entropy) we use to describe their manifestations. As Gibbs goes on to say wryly:

> Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care one may hope, in the main, to avoid.

Having thus clarified that his endeavor concerns a matter of reason rather than empirical certainty, he reserves to the final chapter the question of applying his approach to "systems composed of a number of entirely similar particles, or, it may be, of a number of particles of several kinds, all of each kind being entirely similar to each other." He wished "to separate sharply the purely thermodynamic laws from those special modifications which belong rather to the theory of the properties of matter." The question remains whether his consideration of "entirely similar particles" represents the pinnacle of Gibbs' reasoning or the point beyond which his reasoning can proceed no further without invoking an hypothesis about "the constitution of material bodies." Though this question is not fully decidable, we suggest that propounding "entirely similar particles" entails framing a hypothesis of great significance, one that will bear crucially on the properties of matter.

The first point that he considers is how to speak of the "phases" of such systems, by which he means "conditions with respect to configuration and velocity" (the modern "phase space"). Here, the question of counting the configurations of the identical particles comes to the fore:

> If two phases differ only in that certain entirely similar particles have changed place with one another, are they to be regarded as identical or different phases? If the particles are regarded as indistinguishable, it seems in accordance with the spirit of the statistical method to regard the phases as identical.

One notes that, in his use of the telling phrase "entirely similar," Gibbs has set aside any possibility of the sort he entertained in 1876 that the particles might somehow be similar in themselves but differ in their fields. This confirms the stronger sense of identicality that he had adumbrated in his earlier work. Gibbs goes on to call the phase of the system in which the exchange of similar particles is regarded as changing the phase the *specific phase*, while the phase in which such exchanges are not regarded as changing the phase the *generic phase*. By his last statement, he clearly indicates that the generic phase is the physically significant one. Here is the crucial step, for the number of specific phases of $n_1, n_2, n_3, \ldots$ identical species of particles in a given generic phase is given by $n_1!n_2!n_3!\cdots$. Because of this factor the entropy of the gas divided by a membrane will not increase when the membrane is removed, although Kastler has noted that this factor is only true in the classical limit and thus is only the beginning of a more general quantum consideration.[11] However, Gibbs' articulation of the concept of generic phase and his hypothesis that only it has physical significance gave an enhanced status to his notion of "*entirely* similar particles." Henceforward, true and complete indistinguishability is the key to a proper statistical mechanics and thus is the evident path that the physics of the atom must take.

Gibbs emphasized that, even though the atoms in a given system are quite indiscernible, the different members of a Gibbsian *ensemble* are perfectly distinct and can be individually labeled. As Schrödinger later emphasized, this approach separates ingeniously the question of the indistinguishability of the atoms from the individuality of the members of the ensemble.[12] It is a great tribute to Gibbs' sagacity that, in choosing this approach, he left the way open for quantum statistics. Indeed, he went sufficiently far in that direction by his considerations regarding indistinguishability so that the edifice of his work still stands today.[13]

IV. A BRIEF SURVEY OF WRITINGS AFTER GIBBS

Though we have only considered Gibbs' own arguments in this paper, it should be noted that controversy over the nature and resolution of the "paradox" has not ceased. Von Neumann showed that, in quantum theory, the entropy change between gases may be made to vanish continuously if the gases concerned differ only in their quantum states and if the difference between the states were made to vanish continuously. Klein has discussed this approach and given examples; Landé used it in his reformulation of quantum theory.[14] On the other hand, Bridgman argued that there is a necessary discontinuity in the operational approach to distinguishable as opposed to indistinguishable particles; Boyer amplified this approach to include the times required for such mixing processes and Rosen has discussed the general problem of determining operationally whether systems are identical.[15] Landsberg and Tranah have argued that the arguments of Bridgman and Boyer are not sound since a quasicontinuous sequence of states can be constructed, which go from distinguishable to indistinguishable gas systems, even though the act of making the particles indistinguishable is discontinuous.[16]

A particularly important insight stems from the work of Ehrenfest and Trkal, who questioned the presumption that entropy must be an extensive quantity which underlies most modern resolutions of the paradox.[17] They pointed out that no reversible process can generate changes in the number of gas particles and hence that the entropy difference in such cases is not clearly defined. With this in mind van Kampen argued that quantum mechanics has no bearing on the paradox, which he asserts can be resolved even in classical theory through a purely operational definition of indistinguishability; this argument was also stated trenchantly by Grad much earlier.[18] Such a definition depends wholly on the decision of the observer as to what shall count as "identical." This line of argument has been followed to argue that although identical states seem inherent to quantum theory, there remains the operational possibility for the experimenter to ignore the difference between gases. Thus van Kampen has argued that "the Gibbs paradox is no different in quantum mechanics, it is only less manifest." Although the correct factor of $1/n!$ emerges naturally in the quantum mechanical treatment of the partition function, Ehrenfest and Trkal already realized that one could always bring the partition function into its old form by weighting each state by a factor of $n!$, which is artificial though legitimate.[19] Home and Sengupta have extended these arguments to adduce a continuous dependence of thermodynamic properties on a distinguishability parameter.[20] However, Dieks and van Dijk have pointed out that if the quantum states are not orthogonal an entropy of mixing cannot be strictly defined because such mixing is irreversible.[21] This would restrict the complete generality of the arguments put forward by von Neumann and would support the contention that the Gibbs paradox is not fundamentally alleviated by quantum mechanics.

Although van Kampen has described the arguments of Gibbs as "somewhat mystical" it remains clear that they drew Gibbs to fundamental considerations of indistinguishability which remain of central importance. In the following paper, we shall consider how Planck, de Broglie, Schrödinger, and Einstein picked up the threads of these considerations and how they affected the formation of quantum theory.

ACKNOWLEDGMENTS

This paper was stimulated by discussions in the study group on quantum theory at St. John's College in Santa Fe. I thank my colleagues P. Le Cuyer, J. Steadman, R. Swentzell, and H. von Briesen for helpful discussions. I also thank E. M. Purcell for his encouraging suggestions, as well as M. J. Klein and P. Le Cuyer for their comments on the manuscript. I am indebted to E. T. Jaynes for kindly showing me his unpublished work on the Gibbs paradox from which I have learned much. I wish also to thank St. John's College and the Alfred P. Sloan Foundation for their support.

---

[1] A helpful summary of important points in the development of this idea can be found in M. Jammer, *The Conceptual Development of Quantum Mechanics* (McGraw-Hill, New York, 1966), pp. 338–345.

[2] J. Dalton, *A New System of Chemical Philosophy* (J. Waele, London, 1842), p. 142, quoted in *A Source Book in Chemistry 1400–1900*, edited by H. M. Leicester and H. S. Klickstein (Harvard U.P., Cambridge, 1963), p. 216.

[3] L. Boltzmann, *Theoretical Physics and Philosophical Problems* (Reidel, Dordrecht, 1974), pp. 228–231.

[4] Available in *The Collected Works of J. Willard Gibbs* (Yale U.P., New Haven, 1957), Vol. 1, pp. 165–168.

[5] F. Reif, *Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), pp. 243–246; W. Yourgrau, A. van der Merwe, and G. Raw, *A Treatise on Irreversible and Statistical Thermodynamics* (Macmillan, New York, 1966), pp. 235–241.

[6] Reference 4, p. 166.

[7] J. C. Maxwell, *A Treatise on Electricity and Magnetism* (Dover, New York, 1954), Vol. 1, pp. 62–70, 165–168; H. Hertz, *Electric Waves* (Dover, New York, 1962), pp. 20–28; see also A. M. Lesk, "On the Gibbs paradox: What does indistinguishability really mean?" J. Phys. (London) A **13**, L111–L114 (1980).

[8] J. W. Gibbs, Ref. 4, Vol. 2, pp. 187–207; reprinted in J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Dover, New York, 1960).

[9] L. P. Wheeler, *Josiah Willard Gibbs: The History of a Great Mind* (Yale University, New Haven, 1962), pp. 157, 152. A valuble discussion of the development of Gibbs' ideas can be found in M. J. Klein, "The scientific style of J. W. Gibbs," in *Springs of Scientific Creativity*, edited by R. Aris, H. T. Davis, and R. H. Stuewer (University of Minnesota, Minneapolis, 1983), pp. 142–162.

[10] J. W. Gibbs, Ref. 8, p. ix.

[11] F. Reif, Ref. 5; see A. Kastler's valuble historical survey, "On the historical development of the indistinguishability concept for microparticles," in *Old and New Questions in Physics, Cosmology, and Theoretical Biology*, edited by A. van der Meerwe (Plenum, New York, 1983), pp. 607–623. E. T. Jaynes has drawn my attention to the absence of any reference to extensivity in Gibbs' own considerations (private communication).

[12] E. Schrödinger, *Statistical Thermodynamics* (Cambridge U.P., Cambridge, 1967), pp. 3–4.

[13] P. S. Epstein, "Gibbs' methods in quantum statistics," in *A Commentary on the Scientific Works of J. Willard Gibbs*, edited by A. Haas (Yale University, New Haven, 1936), Vol. 2, pp. 521–577.

[14] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton U.P., Princeton, 1955), pp. 370 ff; M. J. Klein, "Note on a problem concerning the Gibbs paradox," Am. J. Phys. **26**, 80–81 (1958); M. J. Klein, "Remarks on the Gibbs paradox," Ned. T. Natuurk. **25**, 73–76 (1959); A. Landé, *New Foundations of Quantum Theory* (Cambridge U.P., Cambridge, 1965), pp. 61–75; A. M. Lesk, Ref. 7; G. Fay, "Notes on the quantum-mechanical discussion of the Gibbs paradox," Act. Phys. Hung. **18**, 273–283 (1965).

[15] P. W. Bridgman, *The Nature of Thermodynamics* (Harper, New York, 1961), pp. 168–169; T. H. Boyer, "Sharpening Bridgman's resolution of the Gibbs paradox," Am. J. Phys. **38**, 771–773 (1970); R. Rosen, "The Gibbs' paradox and the distinguishability of physical systems," Philos. Sci. **31**, 232–236 (1961); another aspect of the preparation of microscopic and macroscopic states is discussed by B. M. Casper and S. Freier, " 'Gibbs Paradox' paradox," Am. J. Phys. **41**, 509–511 (1973).

[16] P. T. Landsberg and D. Tranah, "The Gibbs paradox and quantum gases," Am. J. Phys. **46**, 228–230 (1978).

[17] P. Ehrenfest and V. Trkal, "Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this," Proc. Acad. Amsterdam **23**, 162–183 (1920), reprinted in P. Ehrenfest, *Collected Scientific Papers* (North-Holland, Amsterdam, 1959), pp. 414–435; see the excellent discussion in M. J. Klein, "Ehrenfest's contributions to the development of quantum statistics," Proc. Acad. Amsterdam B **62**, 41–62 (1959).

[18] H. Grad, "The many faces of entropy," Comm. Pure Appl. Math. **14**, 323–353 (1961), and N. G. van Kampen, "The Gibbs paradox," in *Essays in Theoretical Physics, in Honour of Dirk ter Haar*, edited by W. E. Parry (Pergamon, Oxford, 1984), pp. 303–312; see also W. Gough and J. P. G. Richards, "Distinguishability in the teaching of statistical mechanics," Eur. J. Phys. **2**, 82–85 (1981), W. T. Grandy, Jr., "Indistinguishability, symmetrisation and maximum entropy," Eur. J. Phys. **2**, 86–90 (1981); and R. N. Sen, "The Gibbs paradox," J. Math. Phys. Sci. (India) **17**, 495–500 (1983).

[19] See Ref. 17 and H. Rechenberg, "Ist das Gibbssche Paradoxon paradox?" Phys. Bll. (Ger) **31**, 456–470 (1975); see also A. G. McLellan, "The classical limit of the partition function in statistical mechanics," Am. J. Phys. **40**, 704–709 (1972).

[20] D. Home and S. Sengupta, "Extensivity of entropy and modern forms of the Gibbs paradox," Pramana **17**, 509–514 (1981).

[21] D. Dieks and V. van Dijk, "Another look at the quantum mechanical entropy of mixing," Am. J. Phys. **56**, 430–434 (1988).