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## LETTER TO THE EDITOR

# On the Gibbs paradox: what does indistinguishability really mean?

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**Abstract.** The Gibbs paradox concerns the entropy of mixing of ideal gases: although the entropy change of mixing samples of different gases is unequal to the entropy change of mixing samples of the same gas, it is not clear within the framework of classical thermodynamics how the identity of the particles affects the analysis. An explicit examination of the concept of indistinguishability can clarify some of the implications of the quantum-mechanical resolution of the Gibbs paradox.

In the simplest case of the Gibbs paradox, a partition divides a rigid, thermostated vessel into two chambers of equal volume. Suppose that one chamber contains a mole of argon and the other a mole of krypton, at sufficiently low pressure that deviations from ideality are negligible. If the partition is removed, the gases mix at constant temperature and pressure, with an entropy change  $\Delta S = 2R \ln 2$ . But if the chambers initially contained samples of the *same* gas, the entropy change would be zero.

In his memoir, *On the Equilibrium of Heterogeneous Substances*, J Willard Gibbs stated the following hypothesis: '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. 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.' (Willard Gibbs 1948).

The *discontinuous* change in  $\Delta S$ —from  $2R \ln 2$  to 0—as the gases pass *continuously* from distinguishable to indistinguishable is Gibbs' paradox.

From the quantum-mechanical point of view, this difference in the entropy change arises from the fact that *many states* of a system of distinguishable particles correspond to *a single state* of a system of indistinguishable particles. This is a consequence of the requirement that the wavefunctions of many-identical-particle systems obey symmetry restrictions. The effect is to reduce the number of accessible quantum states of the mixed system, lowering the entropy of the final thermodynamic state. In this way, quantum mechanics provides a microscopic explanation for the difference in entropy of mixing in the cases of distinguishable and indistinguishable particles. But the question of whether *partial* indistinguishability is indeed possible, in practice or even in theory, or whether, alternatively, indistinguishability is necessarily an 'all-or-none' phenomenon, is a more subtle one.

Some authors have asserted, without feeling further comment to be necessary or useful, that two particles are either the same or they are different. Others, following von

Neumann (1955) and Schrödinger (1950, 1952), have used the overlap of wavefunctions representing two quantum states as a *continuous* measure of indistinguishability. Indeed, von Neumann showed that the existence of a semipermeable membrane that would transmit one state and reflect another is consistent with the second law of thermodynamics if and only if the states are orthogonal. Note that this implies the equivalence of the following two senses of the word indistinguishability:

(a) mechanical indistinguishability = the infeasibility of constructing a semipermeable membrane or any other device that can effect a separation of the two types of particles, and

(b) symmetry-restriction indistinguishability = the requirement that many-particle wavefunctions be either symmetric (bosons) or antisymmetric (fermions) to the exchange of equivalent particles.

M J Klein analysed the mixing of two substances containing nuclei in different energy levels. He developed von Neumann's use of the overlap as a continuous measure of indistinguishability, by calculating the value of the entropy of mixing as a function of the overlap of the states of the particles that are mixed. He showed explicitly that the entropy change varies *continuously* from  $0.2R \ln 2$  as the overlap decreases from unity to 0 (Klein 1948, 1959).

These discussions show that the overlap of wavefunctions describing states is the proper quantum-mechanical criterion for indistinguishability, and that, contrary to the second quoted sentence of Gibbs' hypothesis, the entropy of mixing is *not* independent of the degree of similarity.

Although these results contain a formal solution of the Gibbs paradox, an explicit examination of the concept of indistinguishability can make the ideas more concrete, and reveal certain of their implications.

Like other thermodynamic properties, the entropy of a system depends on the distribution of allowed energy levels. In mixing ideal gases at constant temperature and pressure, the entropy change arises from the change in the contribution of the *translational* energy levels to the entropy of the system in the initial and final states. The *internal* energy levels, which in the case of ideal gases are unaffected by the mixing, seem irrelevant.

However, in many cases at least it is the set of internal energy levels that *defines* the distinguishability of two sets of particles. The effect of internal states on indistinguishability was analysed from the point of view of the applicability of the Pauli principle, by Ehrenfest and Oppenheimer (1931). They showed that a wavefunction describing two bound 'clusters' composed of the same subparticles is subject to symmetry restrictions if and only if the clusters have the same internal state, provided that the energy of interaction between the clusters is negligible compared with the difference between energy levels of the individual clusters, a condition that will certainly hold in the ideal gaseous state in which the interaction between particles is zero. Reinterpreting this conclusion in terms of the mechanical sense of the term indistinguishability, it is the ignoring of the internal states that creates Gibbs' paradox.

Let us consider examples in which indistinguishability can be seen to reside not in the identity of the particles themselves, but in the set of accessible quantum states. These examples will suggest that:

(a) There is an element of convention in regarding particles as distinguishable or indistinguishable—what in these cases is indistinguishable is not the particles themselves but their sets of allowed states.

(b) To decide whether the first sentence of Gibbs' hypothesis is true or false, (that is, whether partial indistinguishability is really feasible), one must examine not the particles themselves but the restrictions on transitions between sets of allowed energy levels.

Consider the mixing at constant temperature and pressure of dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) and its isomer ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), in ideal gaseous states. To the chemist, these molecules are distinguishable. However, because they are isomers it is legitimate to regard any state of either molecule as a state of a system consisting of two carbon atoms, six hydrogen atoms; and an oxygen atom. We may *choose* to regard these systems either as *distinguishable* particles (molecules) with individual and independent sets of quantum states, or as *indistinguishable* particles (atoms) occupying different regions of phase space separated by activation energy barriers.

The fact that we may consider the particles as indistinguishable cannot alter the entropy change  $\Delta S = 2R \ln 2$  and not 0 because the *states* of the mixed system are distinguishable. Two states differing only by the exchange of an ether molecule with an ethanol molecule are different by virtue of the difference in the *internal states* of the 8-atom system despite the fact that the same translational levels are occupied.

Consider next the mixing of molecular deuterium ( $\text{D}_2$ ) with helium. Again the particles are distinct and noninterconvertible species. However, every quantum state of  $\text{D}_2$  or He is some state of a system consisting of two protons, two neutrons, and two electrons. Again, the distinguishable particles are composed of the same set of indistinguishable ones, and it is the different internal energy levels that distinguish them.

For the ether-ethanol system the largest indistinguishable subparticles are atoms, but for deuterium-helium they are electrons, protons, and neutrons. This could be carried further. If we regard protons and neutrons as different isospin states of the nucleon, we are then conceding that still another level of apparent distinguishability resides in the state, rather than in some general idea of particle identity. If the question of what particles are ultimately distinguishable is equivalent to the question of what particles are 'elementary', we should not expect a clear-cut answer to either question.

In his discussion of the mixing of two isomeric states of the same nucleus, M J Klein analysed the entropy change in terms of heat exchange with the surroundings, recognising the contribution of the entropy change of the surroundings. However, such heat exchange is not a necessary feature of the mixing of particles that we regard as different states of the same system. Consider the mixing of two enantiomers. By symmetry, the two molecules must have the same energy level distributions, and hence the same thermodynamic properties. But their interconversion at constant temperature in the ideal-gaseous state would involve no heat exchange with the surroundings.

Directing attention to the set of accessible energy levels clarifies the question of whether indistinguishability is an 'all-or-none' phenomenon. Consider a molecule that has an internal rotational barrier between two conformations. At low temperatures, it is possible to imagine separate samples containing pure conformational isomers, each executing torsional vibrations. In the higher-energy states of this system, internal rotation occurs, and no distinction between isomers is possible. These molecules *share* a certain portion of the accessible quantum states (the high-energy states), and retain sole title to others (the low-energy states). In calculating the partition function and the entropy of this system, the higher-energy (internal-rotational) states are reduced in number by permutational symmetry, but the lower-energy (torsional-vibrational) states are *not* reduced in number by permutational symmetry. (We could also say that

ether and ethanol share certain very highly excited states; namely, those in which the molecules are dissociated into the same fragments. These states may be ignored at ordinary temperatures, because they are negligibly populated.)

In computing the entropy change of mixing of samples of conformational isomers, the shared energy levels constitute a *partial* indistinguishability that *does* reduce the entropy change, but not to an observable extent.

Contrary to Gibbs' hypothesis, the existence of pairs of substances that are 'partially indistinguishable' to a significant extent seems unlikely. If two species share non-negligibly populated energy levels, transitions between the two sets of internal states would occur at a high rate. The shared states would thus serve as transition states for the interconversion of the putatively distinct species. On the other hand, if the rate of interconversion is sufficiently slow to justify discussion of an equilibrium mixture of 'distinguishable' species, then the common energy levels cannot be populated sufficiently to cause an observable effect on the entropy change.

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