

Letter

Gibbs' Paradox in the Light of Newton's Notion of State

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Abstract: In this letter, it is argued that the correct counting of microstates is obtained from the very beginning when using Newtonian rather than Laplacian state functions, because the former are *intrinsically* permutation invariant.

Keywords: Gibbs' paradox; classical statistical mechanics of indistinguishable particles; state

Consider the classical mixing entropy, in particular the following case of "two identical fluid masses in contiguous chambers" ([1], Ch. XV, p. 206). "The entropy of the whole is equal to the sum of the entropies of the parts, and double that of one part. Suppose a valve is now opened, making a communication between the chambers. We do not regard this as making any change in the entropy, although the masses of gas or liquid diffuse into one another, and although the same process of diffusion would increase the entropy, if the masses of fluid were different." ([1], Ch. XV, pp. 206 f.)

The paradox consists in that the Lagrange-Laplacian notion of state (comprising the dynamical variables positions *and* velocities or momenta of all bodies involved [2]) *does* predict a *change* in entropy, because it counts the interchange of two "identical" particles as representing two *different* states—at variance with the experimental outcome and with Gibbs' writing quoted above.

This situation suggests to seek a state description, where the state is *not* changed by the opening of the valve above. In other words, the state description should be invariant against the interchange of equal bodies. As a matter of fact, such a state description has been used—among others—by Newton [3].

According to the laws of motion in his *Principia* [4], the state of a body is given by its momentum vector, \vec{p} . In case of several bodies without external interaction, their total momentum,

$$\vec{p}_{tot} = \vec{p}_1 + \vec{p}_2 + \dots$$
 (1)

is conserved. And it is invariant against the interchange of bodies of equal mass if $m_2 = m_1$.

$$\vec{p}_{tot} = m_1 \left(\vec{v}_1 + \vec{v}_2 \right) + \dots$$
(2)

Analogously, the classical Hamiltonian is invariant against the interchange of bodies of equal mass, charge, etc. And because the thermodynamic equilibrium of a Gibbsian ensemble is determined by the Hamiltonian of the system under consideration ([1], Ch. I), it is invariant either. The factor 1/N! is thus *not* due to the (questionable) indistinguishability of quantum particles, but due to the permutation invariance of the *classical* Hamiltonian.

In other words, Lagrange-Laplacian state functions do *not* predict the experimentally observed behaviour, while Newtonian ones do. This suggests that it is *not* the states of *motion* which determine the statistics, but the *stationary* states. As a matter of fact, Einstein [5] has shown, that Planck's quantum distribution law is a consequence of the *discrete* energy spectrum of a Planck resonator (quantum oscillator), while the classical distribution law results from the *continuous* energy spectrum of a classical oscillator. It is noteworthy that (in)distinguishability does not play any role here.

How does this reasoning manifest itself in the counting of micro-states?

Consider the textbook case of 2 fair coins and the 4 possible results of one fair toss (H = head, T = tail).

case	coin 1	coin 2	MB	BE	FD
1	Н	Н	$\frac{1}{4}$	$\frac{1}{3}$	0
2	mdH	mdT	$\frac{1}{4}$	1	1
3	mdT	mdH	$\frac{1}{4}$	$\frac{1}{3}$	1
4	Т	Т	$\frac{1}{4}$	$\frac{1}{3}$	0

Maxwell-Boltzmann (MB) statistics assigns to each of the 4 cases the probability of 1/4. Bose-Einstein (BE) statistics considers the cases 2 and 3 to be one and the same, and assigns to each of the 3 remaining cases the probability of 1/3. Fermi-Dirac (FD) statistics also considers the cases 2 and 3 to be one and the same and, additionally, forbids the cases 1 and 4 (Pauli ban).

Now, as outlined above, from the viewpoint of Newtonian (stationary) states, the cases 2 and 3 are "*automatically*" one and the same. In other words, "Newtonian counting"—though being entirely *classical*—yields BE, i.e., *quantum* statistics. Similar conclusions have been drawn by Bach [6] along another route of reasoning.

In summary, Gibbs' paradox concerning the mixing entropy can be resolved completely within *classical* physics (*cf.* [6][7][8]). This result is important for the self-consistency of classical statistical mechanics [9] as well as for the unity of classical physics [10].

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