# How applicable is Maxwell-Boltzmann statistics?

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In a recent article[1], Enders raised queries concerning the existence of physical systems which obey Maxwell-Boltzmann statistics. Here the question is considered from a different angle and answers are proposed which support the existence of such statistics within the framework of physics.

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Recently[1], Enders, following an argument of Gibbs, claimed that Maxwell-Boltzmann statistics did not apply to classical gases. It was claimed further that the said statistics apply only to ordered sets of distinguishable elements and the query of whether or not such sets exist in physics was raised. It was pointed out that, according to Gibbs, the interchange of two entirely similar particles does not change the phase of an ensemble and so, are not counted as different for calculating such quantities as the entropy. It was pointed out also that, in Maxwell-Boltzmann statistics, equal particles may assume the same state but, for classical particles, although this is possible if the state is defined via the velocity or momenta alone, it is not possible for any situation where the state is given through position and either velocity or momentum. The latter description is the one used by such as Lagrange and Hamilton.

One further important point was included at the very end of the article and that is the claim that Gibbs' paradox shows that the correct counting for classical gases is Bose's counting which yields the Bose-Einstein statistics. This point, if true, would have serious consequences for physics and, consequently, is addressed here also.

It should be admitted from the outset that the ideal quantum gases are not meant to be real gases but, rather, approximations to such. However, over the years these simple models have proved very successful in describing some physical situations; the ideal Fermi gas has dealt competently with electrons in metals and with the description of white dwarf stars, while the ideal Bose gas's condensation phenomenon[3] has helped give insight into the properties of liquid $^4$He. Hence, although concerned with somewhat unrealistic ideal situations, both models have served science well.

In the case of the ideal Fermi gas, the examples quoted both refer to the degenerate state of such a gas and, as has been shown[2], the first case holds when the relation between density *n* and absolute temperature *T* is

$$n \gg 3.71 \times 10^{15} T^{3/2}\ \mathrm{cm}^{-3} \tag{1}$$

whereas, in the white dwarf case, these variables must satisfy

$$n \gg 2.871 \times T^{3}\ \mathrm{cm}^{-3}. \tag{2}$$

In both cases, the numerical values refer specifically to an electron gas.

As was shown in the same reference, the so-called non-degenerate situation applies when the same two variables, *n* and *T*, are related by

$$n \ll 4.8 \times 10^{15} T^{3/2}\ \mathrm{cm}^{-3}. \tag{3}$$

This non-degenerate situation is, of course, what might be termed the classical approximation for either type of ideal quantum gas and refers, therefore, to the case commonly described by Maxwell-Boltzmann statistics. Hence, if Maxwell-Boltzmann statistics are unphysical, the above relations, especially (1) and (3), would imply values of *n* and *T* for which neither type of quantum gas could exist. However, it is known that, to a very good approximation, the so-called classical gas does exist in the laboratory. This is seen regularly in demonstrations of the validity, within acceptable limits of experimental error, of such well-known laws as Boyle's Law and Charles' Law. No-one would claim these to be exact but they, and other results, are known to be approximately valid and are, incidentally, explainable in terms of Maxwell-Boltzmann statistics. It does seem that it is verifiable experimentally that the ideal quantum gases do exist, at least approximately, over an exceptionally wide range of values of both *n* and *T* and certainly over a range covering all the inequalities listed above.

It is not without interest at this point to note that Zemansky considers ideal gases at length in his book[4]. He goes to great lengths to show how real gases may be approximated by the ideal gas model under certain reasonably stringent conditions. This goes some way to confirming the assertion made above relating to some fairly well-known laws commonly met in school physics laboratories.

All this shows that the answer to the question posed by Enders[1] is quite definitely 'Yes; there are physical systems which obey Maxwell-Boltzmann statistics'. This answer may actually refer to limiting cases which are not exactly fulfilled in practice but, as every A-level physics student should know from practical experience, within the limits of experimental error gases in certain prescribed conditions do obey the so-called perfect gas laws.

Of course, as always when dealing with physical systems, great care must be exercised with mathematical arguments. Mathematical argument[5] shows quite clearly that there are only three types of particle allowable in physics and they are fermions, bosons and so-called classical particles. The argument leading to this result is purely mathematical, relying on knowledge of distributions. It was, in fact, shown quite clearly that the stationary probability distributions of so-called intermediate statistics are not compatible with any mechanism which allows variation between Fermi-Dirac and Bose-Einstein statistics. The binomial and negative binomial distributions, characterising Fermi-Dirac and Bose-Einstein statistics, respectively, transform into the Poisson distribution, descriptive of classical statistics, as the number of energy cells increases without limit. These distributions were shown to be the laws of error leading to the average value as the most probable value. Hence, it has been shown quite clearly under what mathematical circumstances classical statistics applies and this has been verified in the laboratory on numerous occasions.

Finally, we consider the Gibbs paradox. Despite its seeming to have been resolved many years ago papers continue to be published on the topic. Indeed, Enders himself[7] has contributed to the debate with an article in which he shows that BE statistics arise not from considerations of indistinguishability, which he calls "questionable", but from the definition of a state, which he chooses to be invariant under permutation of the particles. Enders' contribution to the Gibbs paradox is but one of many that continue to be published. It resolves the paradox, but through the implication that classical systems should be considered as BE systems. We have argued that the evidence does not support this view and that there are indeed many systems that obey, at least approximately, Maxwell-Boltzmann statistics. We have considered mainly gaseous systems, but equally we could have considered dilute solutions or colloidal systems which exhibit Brownian motion. The latter is particularly interesting, not only because the motion of one Brownian particle is essentially independent of any other but because such systems have also been considered in the light of the Gibbs paradox[8]. Swendsen argues that the colloidal Gibbs paradox shows that the currently accepted definition of entropy is incorrect and that in fact Boltzmann's definition of entropy, based of course on Boltzmann statistics, is correct. This is yet another resolution of the Gibbs paradox, different from that of Enders, and with diametrically opposite implications. Thus, Enders' is only one of many solutions to the Gibbs paradox. It is neither unique nor necessarily correct and the overwhelming evidence is to the effect that many physics systems obey classical statistics.

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