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Extensivity of entropy and modern form of Gibbs paradox

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Abstract. The extensivity property of entropy is clarified in the light of a critical examination of the entropy formula based on quantum statistics and the relevant thermodynamic requirement. The modern form of the Gibbs paradox, related to the discontinuous jump in entropy due to identity or non-identity of particles, is critically investigated. Qualitative framework of a new resolution of this paradox, which analyses the general effect of distinction mark on the Hamiltonian of a system of identical particles, is outlined.

Keywords. Extensivity of entropy; Gibbs paradox; distinguishability; identical particles; Hamiltonian.

1. Introduction

In this paper we first examine the expression for entropy of a system of N non-interacting particles in the high temperature-low density limit, as given by Bose-Einstein (B-E) and Fermi-Dirac (F-D) statistics. We point out that for a finite N-particle system, the formula for entropy has a valid term non-proportional to N, which is given by $(k/2) \ln N$. The usual arguments put forward for the neglect of this term have been critically scrutinized. Then the question arises whether such a term, non-proportional to N in the entropy formula, leads to any genuine contradiction with thermodynamics. This necessitates a careful analysis of the thermodynamic requirement regarding the extensivity property of entropy, which is dealt with in § 3. We conclude that thermodynamics demands only that part of entropy to be proportional to N which depends on the thermodynamic variables; hence the term $(k/2) \ln N$ in the entropy formula based on quantum statistics does not contradict any thermodynamic principle. The widely prevalent notion that the formula for entropy based on the concept of distinguishability presents conceptual contradiction with thermodynamics essentially due to the presence of a term non-proportional to N (Gibbs paradox in its old form) is shown to be incorrect. In § 4, the modern form of the Gibbs paradox, regarding the apparent discontinuous jump in the entropy value as distinction marks are ascribed in a system of identical particles, is discussed. Explanations proposed so far have been critically reviewed and the basic ideas of a new resolution are suggested with a view to providing deeper qualitative insight into this paradox.