Gibbs Paradox and the Relation between Thermodynamics and Quantum Theory

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Abstract:

The so-called Gibbs paradox in thermodynamics is concerned with the possible increase of entropy when mixing various (ideal) gases or liquids. In particular, it points to the difference between a process of mixing two distinct gases (nonzero entropy increase) and a process of mixing two quantities of the same gas (zero entropy increase). It has often been argued that the Gibbs paradox reveals a "defect" in classical physics and requires quantum theory, for a satisfactory microphysical underpinning. According to such an argument, thermodynamics cannot be reduces to a classical microphysical theory, and in fact already imply some aspects of quantum theory, in particular the quantum statistics of identical particles.

I will argue, by means of a historical survey of discussions of the Gibbs paradox, that the understanding of what was paradoxical about it changed considerably. Indeed, until the 1920s, those discussions centered on the discontinuity of the entropy of mixing, as a function of physical/chemical properties. It was only after the formulation of the new rules of quantum statistics that the Gibbs paradox became to be regarded as a puzzle about identity.