

Gibbs paradox in stochastic thermodynamics

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The free energy of a classical system consisting of N -interacting identical particles in contact with a heat bath contains the Gibbs factorial $N!$ in addition to the phase space integration of the Gibbs-Boltzmann factor. This formula can be derived as the classical limit in the quantum statistical mechanics with the assumption that the entropy is given by the Shannon entropy of the density matrix, while $N!$ is missing in the formula when the same formulation is considered for classical systems with the Shannon entropy of the canonical distribution. From this fact, one may understand that $N!$ comes from quantum mechanics. However, this interpretation is not logically correct, because it might be possible that the definition of the free energy is not valid. There are several approaches characterizing the Gibbs factorial in classical systems. Our argument stands on a general principle that thermodynamic quantities are defined by experimentally measurable quantities. That is, whether or not $N!$ appears in the formula should be determined by thermodynamic considerations even in stochastic small systems. Concretely, we show that the free energy can be uniquely determined, up to an additive constant proportional to N , from the two conditions[†]. First, the quasi-static work in any configuration change is equal to the free energy difference. Second, the temperature dependence of the free energy satisfies the Gibbs-Helmholtz relation. In particular, the factor $N!$ is unambiguously found from the work in the quasi-static decomposition of small thermodynamic system with any N . In my talk, I will explain our theory with reviewing several approaches to $N!$.

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