GIBBS PARADOX AND SIMILARITY PRINCIPLE

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Abstract

Edwin Thompson Jaynes (5 July 1922 – 30 April 1998) presented a paper entitled "The Gibbs Paradox" [1] at one of the MaxEnt conferences. Entropy of mixing does not change continuously in the Gibbs paradox (Figure 1a). Let us recall that entropy of mixing of liquids, solids and solutions has been calculated in a similar fashion and the Gibbs paradox can be applied to liquids, solids and solutions in condensed phases as well as the gaseous phase. In his book *Mathematical Foundations of Quantum Mechanics*, John von Neumann provided, for the first time, a resolution to the Gibbs paradox by removing the discontinuity of the entropy of mixing: it decreases continuously with the increase in the property similarity of the individual components (See Figure 1b). On page 370 of the English version of this book, it reads that " ... this clarifies an old paradox of the classical form of thermodynamics, namely the uncomfortable discontinuity in the operation with semi-permeable walls... We now have a continuous transition." Based on information theory considerations, the Gibbs paradox has been resolved by me [2,3] and a new entropy-similarity relationship is given (Figure 1c).

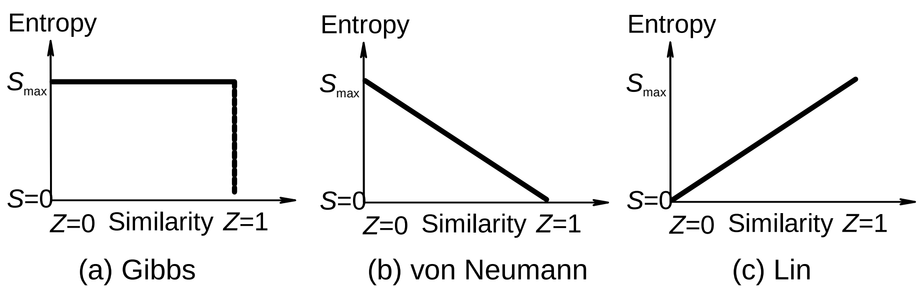

Figure 1. Entropy of mixing and similarity.

Information (I) is defined as the amount of the data after data compression. The first law of information theory: the total amount of data L (the sum of entropy S and information I) of an isolated system remains unchanged. The second law of information theory: Information I of an isolated system decreases to a minimum at equilibrium. The third law of information theory: For a solid structure of perfect symmetry (e.g., a perfect crystal), the information I is zero and the (information theory) entropy (called by me as static entropy for solid state) S is at the maximum. Gibbs Paradox has been resolved. Spontaneously mixed substances at gaseous state can be spontaneously separated at condensed phases (solid or liquid states), driving only by information loss or by the increase in (information theory) entropy. None of the typical pure mixing or separation processes are driving by free energy minimization and the free energy (or total amount of chemical potential) has no change during the processes of ideal mixture formation or ideal mixture separation. The thermodynamic entropy change for the formation of ideal mixtures of gases, liquids or solids is always zero.

A new theory has been proposed as the *Similarity Principle*: If all the other conditions remain constant, the higher the similarity among the components of an ensemble (or a considered system) is, the higher value of entropy of the mixture (for fluid phases) or the assemblage (for a static structure or a system of solid phase) or any other structure (such as an ensemble of quantum states in quantum mechanics) will be, the more stable the mixture or the assemblage will be, and the more spontaneous the process leading to such a mixture or assemblage will be.

References:

[1] For Gibbs paradox literature, see http://www.mdpi.org/lin/entropy/gibbs-paradox.htm

[2] S.-K. Lin, Correlation of entropy with similarity and symmetry. J. Chem. Inf. Comp. Sci. 36, 367-376 (1996).

[3] S.-K. Lin, Gibbs Paradox and the Concepts of Information, Symmetry, Similarity and Their Relationship. Entropy, 10, 1-5 (2008). arXiv:0803.2571.

Key Words: Gibbs paradox, similarity, distinguishability, indistinguishability, stability, spontaneity.