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Abstract

Thermodynamics of Systems with Emergent Molecule Structures †

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Boltzmann entropy is defined as the logarithm of state multiplicity. For multinomial multiplicities, it results in the ordinary Boltzmann-Gibbs-Shannon entropy. However, for non-multinomial systems, we obtain different expressions for entropy. This is the case of complex systems, particularly the case of systems with emergent structures. Probably the most prominent examples of such systems are provided by the chemical reactions with long-range interactions, i.e., where every particle can interact with each other. Based on the original ideas of L. Boltzmann, we calculate the entropy of a system with emergent molecule states. It turns out that the corresponding entropy is the Boltzmann-Gibbs entropy plus a correction that can be interpreted as a structural entropic force. The corresponding thermodynamics is an alternative for the grand-canonical ensemble that correctly counts the number of states. We demonstrate this approach on several examples, including chemical reactions of the type $2X \rightarrow X_2$, phase transitions in a magnetic gas, and the fully connected Ising model. For the fully-connected Ising model, the presence of molecule states shifts the Curie temperature down and changes the order of the phase transition from the second-order to the first order. For systems with short-range interactions, we recover the ordinary Boltzmann-Gibbs entropy and derive the well-known relation between chemical potential and concentration.

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