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Comparison of canonical and microcanonical definitions of entropy

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For more than 100 years, one of the central concepts in statistical mechanics has been the microcanonical ensemble, which provides a way of calculating the thermodynamic entropy for a specified energy. A controversy has recently emerged between two distinct definitions of the entropy based on the microcanonical ensemble: (1) The Boltzmann entropy, defined by the density of states at a specified energy, and (2) The Gibbs entropy, defined by the sum or integral of the density of states below a specified energy. A critical difference between the consequences of these definitions pertains to the concept of negative temperatures, which by the Gibbs definition cannot exist. In this paper, we call into question the fundamental assumption that the microcanonical ensemble should be used to define the entropy. We base our analysis on a recently proposed canonical definition of the entropy as a function of energy. We investigate the predictions of the Boltzmann, Gibbs, and canonical definitions for a variety of classical and quantum models. Our results support the validity of the concept of negative temperature, but not for all models with a decreasing density of states. We find that only the canonical entropy consistently predicts the correct thermodynamic properties, while microcanonical definitions of entropy, including those of Boltzmann and Gibbs, are correct only for a limited set of models. For models which exhibit a first-order phase transition, we show that the use of the thermodynamic limit, as usually interpreted, can conceal the essential physics.

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Keywords: Negative temperature, entropy, canonical, microcanonical

I. INTRODUCTION

The thermodynamic entropy is unique, and provides a complete description of the macroscopic properties of a system[1]. Nevertheless, its definition is still the subject of some dispute. Recently, a controversy has emerged between two distinct microcanonical definitions: (1) The Boltzmann entropy, given by the density of states at a specified energy[2–7], and (2) The Gibbs entropy, given by the sum or integral of the density of states below a specified energy[8, 9]. A critical difference between the consequences of these definitions pertains to the concept of negative temperatures[10–12], which by the Gibbs definition, cannot exist. The advocates of the Gibbs entropy reject negative temperatures, claiming that they are inconsistent with thermodynamic principles [13–19], while other authors have argued that thermodynamics is consistent with negative temperatures, and a different definition of entropy can give correct thermodynamic predictions when the Gibbs entropy does not[20–35].

A related issue that has been raised is whether the limit of an infinite system (thermodynamic limit) is essential to thermodynamics[16–18, 36–39]. We take the position that, while the approximation of an infinite system can be useful for certain calculations, it is also necessary for any theoretical approach to specify how to calculate the thermal properties of finite systems.

For example, a gas in a container that can adsorb particles on its walls has both interesting (non-extensive) physics and practical applications. However, in the limit of an infinite system the contribution of the walls diverges

more slowly than the contributions of the bulk. As the thermodynamic limit is usually represented, the system appears to be extensive, and the effect of the walls is lost. We will show that in a similar way, the thermodynamic limit can obscure the essential physics of first-order transitions, and we suggest an alternate representation of the thermodynamic limit.

It has been claimed that thermodynamics should also apply to systems as small as a single particle[13–18]. While we agree that thermodynamics should apply to finite systems, the predicted measurements of such systems should be unique. This requires a large number of particles so that the measured macroscopic variables have relative fluctuations smaller than the accuracy of the measurement.

The Boltzmann entropy predicts that negative temperatures should occur wherever the density of states is a decreasing function of energy. Since this often occurs in a quantum spin system, the entropy in quantum statistical mechanics is central to the debate. Defining the entropy for a quantum system has the added complexity that energy eigenvalues for a finite system are restricted to a discrete set of energies. It has been recently pointed out that while microcanonical proposals for the entropy are “*a priori* only defined on the discrete set of eigenvalues”[16], the correct thermodynamic entropy, even for quantum systems, must be a continuous function of energy[35]. The key point in this argument is that if a system of interest has ever been in thermal contact with another system, separation will never leave either system in a quantum eigenstate. Consequently, the microcanonical ensemble is not an appropriate tool for calculating the thermodynamic properties of a quantum system.

It was also argued in Ref. [35] that the appropriate probability distribution of quantum systems should be

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