Negative temperatures and the definition of entropy

Robert H. Swendsen [a], Jian-Sheng Wang [b],*

[a] *Physics Department, Carnegie Mellon University, Pittsburgh, PA 15213, USA*
[b] *Department of Physics, National University of Singapore, Singapore 117551, Republic of Singapore*

HIGHLIGHTS

- Gibbs volume entropy is incorrect.
- A new definition of entropy is presented.
- Debate on the existence of negative temperature resolved.

ARTICLE INFO

ABSTRACT

The concept of negative temperature has recently received renewed interest in the context of debates about the correct definition of the thermodynamic entropy in statistical mechanics. Several researchers have identified the thermodynamic entropy exclusively with the "volume entropy" suggested by Gibbs, and have further concluded that by this definition, negative temperatures violate the principles of thermodynamics. We disagree with these conclusions. We demonstrate that volume entropy is inconsistent with the postulates of thermodynamics for systems with non-monotonic energy densities, while a definition of entropy based on the probability distributions of macroscopic variables does satisfy the postulates of thermodynamics. Our results confirm that negative temperature is a valid extension of thermodynamics.

1. Introduction

In 1951, Purcell and Pound, and in 1956, Ramsey, developed the principles of negative temperatures in thermodynamics and statistical mechanics [1,2]. Their analyses have recently been challenged by several authors, who claim that negative temperatures are not consistent with thermodynamics and statistical mechanics [3–15]. The most clearly stated opposition to negative temperatures has been given by Dunkel and Hilbert (DH) [8–12] and Hilbert, Hänggi, and Dunkel (HHD) [13], so we will primarily address their arguments. The claims of these authors are based on the assertion that an expression for a volume entropy, which had been suggested by Gibbs [16], is the only correct definition of entropy in statistical mechanics.

DH and HHD have also claimed that they have extended the domain of thermodynamics to very small systems—even systems with a single degree of freedom. We are very skeptical that any form of thermodynamics can apply to small systems, and we will give our reasons later in this paper. Our main discussion is restricted to many-body systems, which is the usual domain of thermodynamics. We will not require that the system size be infinite, but it should be large enough for the relative thermal fluctuations to be smaller than the experimental resolution. A size of 10^{12} particles, as might be found in a colloid, is usually sufficient.

---

* Corresponding author.
  E-mail address: phywjs@nus.edu.sg (J.-S. Wang).

Aside from the issue of small systems, we have two questions to consider:

1. Are negative temperatures inconsistent with thermodynamics?
2. Is the volume entropy the correct definition of the thermodynamic entropy in statistical mechanics?

As we will demonstrate, the answer to both questions is *no*.

The conclusions of the opponents of negative temperature have already been challenged [17–29]. We especially endorse the arguments given by Frenkel and Warren [21], although we believe that some issues still need to be clarified. Importantly, although the discussion has involved the question of how to properly define the thermodynamic entropy in statistical mechanics, it has failed to include alternative definitions of entropy that call for consideration, as discussed below [30–33].

The main arguments by the authors who oppose negative temperatures and advocate the volume entropy concern violations of adiabatic invariance and related claimed inconsistencies with thermodynamics for a system with a monotonically increasing density of states [9,10,13]. In fact, the violations and inconsistencies they point to are all of order $1/N$, where N is the number of particles, and therefore disappear into the thermal noise, which is of order $1/\sqrt{N}$. An important feature of macroscopic systems is that because thermal fluctuations are so small, a single measurement of E (energy), V (volume), or N will almost certainly produce the average value within experimental resolution. Determining the mean value with a relative error of less than $1/N$ in the presence of fluctuations would require at least N independent measurements, even if each individual measurement were exact. Even for a colloid with only 10^{12} particles, if an independent measurement could be performed every second, it would take over 30,000 years to complete the experiment. The differences that HHD base their arguments on are unmeasurable.

No arguments have been proposed for the volume entropy when the density of states decreases with energy, which is when negative temperatures might arise.

In Section 2, we review the postulates of thermodynamics, and explain the modification needed to include negative temperatures. These postulates are the requirements that must be satisfied by the thermodynamic entropy, and therefore conditions that must be met by an acceptable definition. We discuss the definitions considered by DH and HHD in Section 3, and then review a definition of entropy based on the thermodynamic postulates and the probability of the macroscopic variables in Section 4.

In Section 5, we show explicitly that the inconsistencies noted by DH and HHD are of order $1/N$, and therefore negligible for thermodynamic systems. We also show that there are inconsistencies exhibited by the volume entropy for systems with non-monotonic densities of states, and that these inconsistencies are of order 1 for systems of all sizes.

In Section 6, we demonstrate that the HHD definition of entropy fails to satisfy the zeroth and second laws of thermodynamics. In Section 7, we consider the interactions of a system of non-interacting Ising spins, with an inverted energy distribution, with other such spin systems, or with a system of simple harmonic oscillators. This provides an explicit example of a calculation suggested by Frenkel and Warren for demonstrating that the volume entropy violates the second law of thermodynamics [21]. We discuss the applicability of thermodynamics to small systems in Section 8 before summarizing our conclusions in the final section.

2. Thermodynamic conditions for the definition of entropy

Thermodynamics was invented in the nineteenth century by brilliant scientists who did not make use of the concept of atoms. Most scientists did not believe that molecules existed, much less that they might provide a foundation for the laws of thermodynamics. Clausius saw the necessity of entropy without knowing where it came from or what it might mean. Even after the pioneering work of Boltzmann and Gibbs, many prominent scientists continued to reject a molecular explanation of macroscopic phenomena. Although the existence of molecules is taken for granted today, it should be remembered that the domain of thermodynamics remains that of macroscopic phenomena for which individual atoms are not resolved.

Thermodynamics ignored fluctuations from the start: initially because the existence of fluctuations was not known, but primarily because macroscopic states could be completely characterized by energy, volume, and particle number. The now well-known justification for the neglect of fluctuations is that they are of order $1/\sqrt{N}$, where N is the number of particles in the system, and therefore smaller than the resolution of macroscopic measurements. Even for a small macroscopic system with $N \sim 10^{18}$, thermodynamic measurements rarely have a relative resolution of 10^{-9}.

The requirement that fluctuations are smaller than experimental resolution is fundamental. However, it is not the only requirement. For two objects to be in thermal contact, it is necessary for some sort of direct interaction to exist between particles in different systems. Due to the short range of molecular interactions – perhaps a few nanometers – these interacting particles are found only on the interfaces where the objects come into contact. This implies that the relative size of interactions between three-dimensional objects goes roughly as $N^{-1/3}$. These surface effects can place a stricter limit on the domain of validity of thermodynamics, but one that is still satisfied for macroscopic experiments.

A consequence of these considerations is that thermodynamics is applicable to finite systems, as long as they contain a sufficient number of particles for the fluctuations and the interface effects to be neglected.

At least since the work of Callen, the structure of thermodynamics has been seen to follow logically from a small set of postulates, all of which concern the properties of the thermodynamic entropy [34]. While it will not be necessary to follow the entire development of thermodynamics from these postulates, we will need a subset of them, which we will express in a modified form [32].