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The definition of the thermodynamic entropy in statistical mechanics

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HIGHLIGHTS

- The entropy is defined in agreement with the Callen postulates of thermodynamics.
- The thermodynamic entropy is defined as the log of a normalizable probability.
- The objections of Dieks are analyzed and shown to be incorrect.
- The objections of Peters are analyzed and shown to be incorrect.

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ABSTRACT

A definition of the thermodynamic entropy based on the time-dependent probability distribution of the macroscopic variables is developed. When a constraint in a composite system is released, the probability distribution for the new equilibrium values goes to a narrow peak. Defining the entropy by the logarithm of the probability distribution automatically makes it a maximum at the equilibrium values, so it satisfies the Second Law. It also satisfies the postulates of thermodynamics. Objections to this definition by Dieks and Peters are discussed and resolved.

1. Introduction

Thermodynamics is an extremely successful phenomenological theory of macroscopic experiments. The entropy plays a central role in this theory because it is a unique function for each system that determines all thermodynamic information. The calculation of the form of the entropy lies in the microscopic description given by statistical mechanics. In this paper, I present a simple derivation of the entropy using reasonable assumptions about the probability distributions of macroscopic variables and approximations based on the large number of particles in macroscopic systems.

The basic task of thermodynamics is the prediction of the values of the macroscopic variables after the release of one or more constraints and the subsequent relaxation to a new equilibrium. This appears in the key thermodynamic postulate that is a particular form of the second law [1–3].

> The values assumed by the extensive parameters of an isolated composite system in the absence of an internal constraint are those that maximize the entropy over the set of all constrained macroscopic states [3].

I will show that the solution to this problem in statistical mechanics leads to a function that satisfies this postulate, as well as satisfying the rest of the postulates of thermodynamics. Since these postulates are sufficient to generate all of thermodynamics, and since the thermodynamic entropy is unique [4], this function can be identified as the entropy.

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I have presented other derivations in the past that are equivalent, though perhaps not as direct [5–10]. They have been criticized by Dieks [11,12] and Peters [13,14], whose arguments will be discussed in Sections 5 and 6.

2. The prediction of equilibrium values from statistical mechanics

Thermodynamics is a description of the properties of systems containing many particles (macroscopic systems), for which the fluctuations can be ignored because they are smaller than the experimental resolution. The basic problem of thermodynamics is to predict the equilibrium values of the extensive variables after the release of a constraint in a composite system. I will first consider this as a problem is statistical mechanics, without using any thermodynamic concepts.

Consider a composite system of $M \geq 2$ subsystems, with a total energy E_T, volume V_T, and particle number N_T [15]. Denote the total phase space for this composite system (in three dimensions) by $\{p, q\}$, where p is the $3N_T$-dimensional momentum space, and q is the $3N_T$-dimensional configuration space. Define the probability distribution in the phase space of the composite system as $\phi_T(\{p, q\}, t)$, where t is the time. I will assume that the composite system is initially in equilibrium at time $t = 0$, and that the initial conditions are given by setting ϕ_T equal to a constant, subject to all information available about the system at that time.

Assume that interactions between subsystems are sufficiently short-ranged that they may be neglected [16]. Then, we can write the total Hamiltonian as a sum of contributions from each system.

$$H_T = \sum_{j=1}^{M} H_j(E_j, V_j, N_j). \tag{1}$$

The energy, volume, and particle number of subsystem j are denoted as E_j, V_j, and N_j, subject to the conditions on the sums.

$$\sum_{j=1}^{M} E_j = E_T; \qquad \sum_{j=1}^{M} V_j = V_T; \qquad \sum_{j=1}^{M} N_j = N_T. \tag{2}$$

In keeping with the idea that we are describing macroscopic experiments, assume that no measurements are made that might identify individual particles, whether or not they are formally indistinguishable [17]. This means that there are $N_T!/\left(\prod_{j=1}^{M} N_j!\right)$ different permutations for assigning particles to subsystems, and all permutations may be regarded as equally probable. The probability distribution in the phase space of the composite system is given by

$$\phi_T(\{p, q\}, t = 0) = \frac{1}{\Omega_T}\left(\frac{N_T!}{\prod_{j=1}^{M} N_j!}\right)\prod_{k=1}^{M} \delta\left(E_k - H_k(\{p_k, q_k\})\right), \tag{3}$$

where $\{p_k, q_k\}$ is the phase space for the particles in subsystem k, and Ω_T is a normalization factor. The constraint that the N_k particles in subsystem k are restricted to a volume V_k is left implicit in Eq. (3).

The probability distribution for the macroscopic observables can then be written as

$$W\left(\{E_j, V_j, N_j\}\right) = \frac{N_T!}{\Omega_T}\left(\frac{1}{\prod_j N_j!}\right)\int \mathrm{d}p \int \mathrm{d}q \prod_{j=1}^{M} \delta(E_j - H_j), \tag{4}$$

or

$$W(\{E_j, V_j, N_j\}) = \frac{\prod_{j=1}^{M} \Omega_j(E_j, V_j, N_j)}{\Omega_T / N_T! h^{3N_T}}, \tag{5}$$

where

$$\Omega_j = \frac{1}{h^{3N_j} N_j!}\int_{-\infty}^{\infty} \mathrm{d}p_j \int_{V_j} \mathrm{d}q_j\, \delta(E_j - H_j). \tag{6}$$

The factor of $1/h^{3N_j}$, where h is Planck's constant, is not necessary for classical mechanics. It has been included to ensure that the final answer agrees with the classical limit from quantum statistical mechanics [3].

There is no requirement that the Hamiltonians H_j are the same, so there is also no requirement that the individual Ω_j's have the same functional form. Long-range interactions *within a system* are allowed.

If one or more constraints are now released, the probability $\phi_T(\{p, q\}, t)$ will become time dependent. After sufficient time has passed, the probability distribution will have spread throughout the available phase space, although it will still