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Deriving partition functions and entropic functionals from thermodynamics

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HIGHLIGHTS

- The inverse problem for obtaining the entropic functional is presented.
- We do not make use of the MaxEnt principle.
- An arbitrary probability distribution and an energy spectrum are necessary.
- A mean energy U can be computed and we derive also the partition function Z.
- The entropic functional S and mean energy U satisfy the basic relation $\mathrm{d}U = T\mathrm{d}S$.

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ABSTRACT

Given an arbitrary probability distribution and a nondegenerate energy spectrum, so that a mean energy U can be computed, we derive the partition function Z and the entropic functional S that satisfy the basic relation $\mathrm{d}U = T\mathrm{d}S$. The procedure is illustrated by considering examples of typical distributions found currently in nature. In particular, the power-law spectrum is shown to correspond to a critical state, associated with Tsallis' entropy.

1. Introduction

The first and second laws of thermodynamics are two of physics' foundational statements [1]. In statistical mechanics, an underlying *microscopic substratum* is added that is able to explain thermodynamics itself [2–4]. On this substratum, a probability distribution (PD), that controls the population of microstates, constitutes the fundamental microscopic ingredient [2–4]. The main goal of statistical mechanics is to determine the partition function Z from this PD (or a density matrix), which will permit one to obtain thermodynamic properties. The entropic functional is assumed to be known, of course. Changes that affect exclusively microstate populations give rise to "heat" [2–4]. How these changes are related to energy changes provides an essential content of the first law [2].

Since contemporaneous experimental techniques in complex systems are able to measure energy spectra $\{\epsilon_i\}$ and subsequently, construct their probability distribution $p(\epsilon)$, it would be most desirable to obtain, from such data, the entropic functional associated. Although previous proposals for achieving this purpose exist in the literature [5,6], they were derived

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by means of information theory; herein we will present a method based solely on thermodynamics. In this effort we will discuss the concomitant inverse problem with respect to the standard one mentioned in the previous paragraph. Assuming a PD $p(\epsilon)$ is given from the start, and that you know the pertinent energy spectrum, can one determine, from thermodynamics only, the associated entropic functional $S[p]$ so that the all-important relation $\mathrm{d}U = T\mathrm{d}S$ holds (U is the mean energy evaluated with p)? We show below that the answer is in the affirmative. Our present endeavors are inspired in an illuminating recent work by Hanel, Thurner, and Gell-Mann [6] that used the Bernoulli equation to reconstruct entropies from distribution functions in the context of super-statistics and the maximum-entropy principle. Our contribution here does not appeal to MaxEnt, but to Thermodynamics' first and second laws. Additionally, our approach enables one to get the partition function Z as well, which is not the case in Refs. [5,6].

2. Preliminaries

We need to deal with several sums [7], running over a set of quantum numbers that *completely* identify a given state, collectively denoted by i (the following analysis applies only to nondegenerate energy spectra). The i specify (without ambiguity) an appropriate basis in Hilbert space and $p = \{p_i\}$ is an a-priori given probability distribution such that

$$\sum_i p_i = 1. \tag{1}$$

Sums over i, let us insist, are not necessarily sums over energy states. They are of a more general character. Let f be an arbitrary smooth function of the p_i, satisfying the condition that $pf(p)$ is concave. We assume that, the yet unknown, entropic functional $S[p]$ is of the form

$$S = k\sum_i p_i f(p_i) \tag{2}$$

$$p_i f(p_i) = 0, \quad \text{if } p_i = 1, \tag{3}$$

$$\text{or if } p_i = 0. \tag{4}$$

Our goal is to determine $f(p_i)$. Furthermore, we assume that mean values of quantities A, that take the value A_i with probability p_i, are evaluated according to

$$\langle A\rangle = \sum_i A_i\, g(p_i), \tag{5}$$

with g representing another arbitrary smooth, monotonic function of the p_i, such that $g(0) = 0$ and $g(1) = 1$. Notice that Eq. (5) may be understood as a constraint. We will not necessarily impose the condition $\sum_i g(p_i) = 1$. A particular case for such equation is that of the mean energy U, given by

$$U = \sum_i \epsilon_i\, g(p_i), \tag{6}$$

from which one identifies the standard choice corresponding to $g(p) = p$.

3. The formal solution to the inverse problem

3.1. The direct problem

This problem has been addressed in Ref. [8] (see also Refs. [9,10]). Let us consider a small change in the level populations (which may occur, e.g., due to an infinitesimal exchange of heat); then, the probabilities $\{p_i\}$ will vary according to,

$$p_i \to p_i + \mathrm{d}p_i, \quad \text{with } \sum_i \mathrm{d}p_i = 0, \tag{7}$$

where the last condition comes from Eq. (1). This procedure will in turn, generate infinitesimal changes in the entropy, dS, and internal energy, dU. We want then to make sure that the heat contribution, $\mathrm{d}U = T\mathrm{d}S$, of thermodynamics' first law, is obeyed, so that we impose the condition that, in the above described circumstances,

$$\mathrm{d}U - T\mathrm{d}S = 0, \tag{8}$$

with T representing the temperature. As a consequence of Eq. (8), a little algebra yields, up to first order in dp_i, the condition [8],

$$\sum_i \left(\epsilon_i\, g'(p_i) - kT\left[f(p_i) + p_i f'(p_i)\right]\right)\mathrm{d}p_i \equiv \sum K_i \mathrm{d}p_i = 0, \tag{9}$$

where the primes indicate derivatives with respect to p_i.