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# On the entropy minimization problem in Statistical Mechanics

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ABSTRACT

In many works on Statistical Mechanics and Statistical Physics, when deriving the distribution of particles of ideal gases, one uses the method of Lagrange multipliers in a formal way. In this paper we treat rigorously this problem for Bose–Einstein, Fermi–Dirac and Maxwell–Boltzmann entropies and present a complete study in the case of the Maxwell–Boltzmann entropy. Our approach is based on recent results on series of convex functions.



## 1. Introduction

In Statistical Mechanics and Statistical Physics, when studying the distribution of the particles of an ideal gas, one considers the problem of maximizing

$$\sum_i \left[ n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i}{g_i}\right)\right] \tag{1.1}$$

with the constraints $\sum_i n_i = N$ and $\sum_i n_i \varepsilon_i = E$, where, as mentioned in [5, pp. 141–144], $\varepsilon_i$ denotes the average energy of a level, $g_i$ the (arbitrary) number of levels in the $i$th cell, and, in a particular situation, $n_i$ is the number of particles in the $i$th cell. Moreover, $a = -1$ for the Bose–Einstein case, $+1$ for the Fermi–Dirac case, and 0 for the (classical) Maxwell–Boltzmann case. Even if nothing is said explicitly about the set $I$ of the indices $i$, from several examples in the literature, $I$ is (or may be) an infinite countable set; the examples

$$\varepsilon_l = l(l+1)h^2/2I, \quad g_l = (2l+1); \quad l = 0, 1, 2, \ldots \tag{1.2}$$

$$\varepsilon_{vK} = \varepsilon_0 + h\omega(v + \tfrac{1}{3}) + h^2K(K+1)/2I; \quad v, K = 0, 1, 2, \ldots \tag{1.3}$$

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$$\varepsilon(n_x,n_y,n_z)=\frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2);\quad n_x,n_y,n_z=1,2,3,\ldots \tag{1.4}$$

are considered in [3, p. 76], [4, p. 138] and [5, p. 10], respectively.

Relation (1.1) suggests the consideration of the following functions defined on $\mathbb{R}$ with values in $\overline{\mathbb{R}}$, called, respectively, Bose–Einstein, Fermi–Dirac and Maxwell–Boltzmann entropies:

$$E_{BE}(u):=\begin{cases} u\ln u-(1+u)\ln(1+u) & \text{if } u\in\mathbb{R}_+,\\ \infty & \text{if } u\in\mathbb{R}_-^*,\end{cases} \tag{1.5}$$

$$E_{FD}(u):=\begin{cases} u\ln u+(1-u)\ln(1-u) & \text{if } u\in[0,1],\\ \infty & \text{if } u\in\mathbb{R}\setminus[0,1],\end{cases} \tag{1.6}$$

$$E_{MB}(u):=\begin{cases} u(\ln u-1) & \text{if } u\in\mathbb{R}_+,\\ \infty & \text{if } u\in\mathbb{R}_-^*,\end{cases} \tag{1.7}$$

where $0\ln 0:=0$ and $\mathbb{R}_+:=[0,\infty[$, $\mathbb{R}_+^*:=]0,\infty[$, $\mathbb{R}_-:=-\mathbb{R}_+$, $\mathbb{R}_-^*:=-\mathbb{R}_+^*$. We have that

$$E_{BE}'(u)=\ln\frac{u}{1+u}\ \forall u\in\mathbb{R}_+^*,\quad E_{FD}'(u)=\ln\frac{u}{1-u}\ \forall u\in\,]0,1[,\quad E_{MB}'(u)=\ln u\ \forall u\in\mathbb{R}_+^*.$$

Observe that $E_{BE}$, $E_{MB}$, $E_{FD}$ are convex (even strictly convex on their domains), derivable on the interiors of their domains with increasing derivatives, and $E_{BE}\le E_{MB}\le E_{FD}$ on $\mathbb{R}$. The (convex) conjugates of these functions are

$$E_{MB}^*(t)=e^t\ \forall t\in\mathbb{R},\quad E_{FD}^*(t)=\ln(1+e^t)\ \forall t\in\mathbb{R},\quad E_{BE}^*(t)=\begin{cases} -\ln(1-e^t) & \text{if } t\in\mathbb{R}_-^*,\\ \infty & \text{if } t\in\mathbb{R}_+.\end{cases}$$

Moreover, for $W\in\{E_{BE},E_{MB},E_{FD}\}$ we have that $\partial W(u)=\{W'(u)\}$ for $u\in\operatorname{int}(\operatorname{dom}W)$ and $\partial W(u)=\emptyset$ elsewhere; furthermore,

$$(W^*)'(t)=\frac{e^t}{1+a_We^t}\quad \forall t\in\operatorname{dom}W^*, \tag{1.8}$$

where (as above)

$$a_W:=\begin{cases} -1 & \text{if } W=E_{BE},\\ 0 & \text{if } W=E_{MB},\\ 1 & \text{if } W=E_{FD}.\end{cases} \tag{1.9}$$

The maximization of (1.1) subject to the constraints $\sum_i n_i=N$ and $\sum_i n_i\varepsilon_i=E$ is equivalent to the minimization problem

$$\text{minimize } \textstyle\sum_i g_iW(\frac{n_i}{g_i})\quad \text{s.t. } \sum_i n_i=N,\ \sum_i n_i\varepsilon_i=E,$$

where $W$ is one of the functions $E_{BE}$, $E_{FD}$, $E_{MB}$ defined in (1.5), (1.6), (1.7), and $g_i\ge 1$.

In many books treating this subject (see [4, pp. 119, 120], [3, pp. 15, 16], [5, p. 144], [1, p. 39]) the above problem is solved using the Lagrange multipliers method in a formal way.

Our aim is to treat rigorously the minimization of Maxwell–Boltzmann, Bose–Einstein and Fermi–Dirac entropies with the constraints $\sum_{i\in I}u_i=u$, $\sum_{i\in I}\sigma_iu_i=v$ in the case in which $I$ is an infinite countable set. Unfortunately, we succeed to do a complete study only for the Maxwell–Boltzmann entropy. For a short description of the results see Conclusions.

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