We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter 11

Foundation of Equilibrium Statistical Mechanics Based on Generalized Entropy

A.S. Parvan

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/60997

Abstract

The general mathematical formulation of the equilibrium statistical mechanics based on the generalized statistical entropy for the first and second thermodynamic potentials was given. The Tsallis and Boltzmann-Gibbs statistical entropies in the canonical and microcanonical ensembles were investigated as an example. It was shown that the statistical mechanics based on the Tsallis statistical entropy satisfies the requirements of equilibrium thermodynamics in the thermodynamic limit if the entropic index z=1/(q-1) is an extensive variable of state of the system.

Keywords: Equilibrium statistical mechanics, Tsallis nonextensive statistics

1. Introduction

In modern physics, there exist alternative theories for the equilibrium statistical mechanics [1, 2] based on the generalized statistical entropy [3-12]. They are compatible with the second part of the second law of thermodynamics, i.e., the maximum entropy principle [13-14], which leads to uncertainty in the definition of the statistical entropy and consequently the equilibrium probability density functions. This means that the equilibrium statistical mechanics is in a crisis. Thus, the requirements of the equilibrium thermodynamics shall have an exclusive role in selection of the right theory for the equilibrium statistical mechanics. The main difficulty in foundation of the statistical mechanics based on the generalized statistical entropy, i.e., the deformed Boltzmann-Gibbs entropy, is the problem of its connection with the equilibrium thermodynamics. The proof of the zero law of thermodynamics and the principle of additivity

INTECH
open science | open minds

© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

in general serves as a primarily problem. The equilibrium thermodynamics is a phenomenological theory defined on the class of homogeneous functions of the zero and first order [15].

The formalism of the statistical mechanics agrees with the requirements of the equilibrium thermodynamics if the thermodynamic potential, which contains all information about the physical system, in the thermodynamic limit is a homogeneous function of the first order with respect to the extensive variables of state of the system [14, 6-7]. It was proved that for the Tsallis and Boltzmann-Gibbs statistics [6, 7], the Renyi statistics [10], and the incomplete nonextensive statistics [12], this property of thermodynamic potential provides the zeroth law of thermodynamics, the principle of additivity, the Euler theorem, and the Gibbs-Duhem relation if the entropic index z is an extensive variable of state. The scaling properties of the entropic index z and its relation to the thermodynamic limit for the Tsallis statistics were first discussed in the papers [16, 17].

The aims of this study are to establish the connection between the Tsallis statistics, i.e., the statistical mechanics based on the Tsallis statistical entropy, and the equilibrium thermodynamics and to prove the zero law of thermodynamics.

The structure of the chapter is as follows. In Section 2, we review the basic postulates of the equilibrium thermodynamics. The equilibrium statistical mechanics based on generalized entropy is formulated in a general form in Section 3. In Section 4, we describe the Tsallis statistics and analyze its possible connection with the equilibrium thermodynamics. The main conclusions are summarized in the final section.

2. Equilibrium thermodynamics

2.1. Thermodynamic potentials

In the equilibrium thermodynamics, the physical properties of the system are fully identified by the fundamental thermodynamic potential $f = f(x_1, \ldots, x_n)$ as a real-valued function of n real variables, which are called the variables of state. The macroscopic state of the system is fixed by the set of independent variables of state $x = (x_1, \ldots, x_n)$. Each variable of state x_i, which is related to the certain thermodynamic quantity, describes some individual property of the system. The first and the second partial derivatives of the thermodynamic potential with respect to the variables of state define the thermodynamic quantities (observables) of the system, which describe other individual properties of this system. The first differential and the first partial derivatives of the fundamental thermodynamic potential with respect to the variables of state can be written as

$$df = \sum_{i=1}^{n} u_i dx_i, \qquad u_i = \frac{\partial f}{\partial x_i}, \tag{1}$$

http://dx.doi.org/10.5772/60997

where the vector $u=(u_1, \ldots, u_n)$. Equation (1) is the fundamental equation of thermodynamics and expresses the first law of thermodynamics. The second differential of the fundamental thermodynamic potential is written as a quadratic form

$$d^2 f = \sum_{i=1}^{n}\sum_{j=1}^{n} a_{ij} dx_i dx_j, \qquad a_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j}, \tag{2}$$

where a_{ij} is the element of the symmetric matrix A of the dimension $(n \times n)$. The symmetry conditions for the matrix elements, $a_{ij}=a_{ji}$, lead to the equalities (Maxwell relations)

$$\frac{\partial u_j}{\partial x_i} = \frac{\partial u_i}{\partial x_j} \qquad (i, j = 1, \ldots, n). \tag{3}$$

If the function $f(x_1, \ldots, x_n)$ is convex (concave) on $s \le n$ variables of state, then the quadratic form (Eq. (2)) in s variables is positive definite (negative definite). The quadratic form (Eq. (2)) in s variables for which $a_{ij}=a_{ji}$ is positive definite (negative definite) if [18]

$$a_{11}\xi > 0, \ \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \xi^2 > 0, \ \ldots, \ \begin{vmatrix} a_{11} & a_{12} & \ldots & a_{1s} \\ a_{21} & a_{22} & \ldots & a_{2s} \\ \vdots & \vdots & \ddots & \vdots \\ a_{s1} & a_{s2} & \ldots & a_{ss} \end{vmatrix} \xi^s > 0 \tag{4}$$

for every nonzero vector x, where $\xi=1$ for the positive definite quadratic form and $\xi=-1$ for the negative definite quadratic form. Note that the fundamental thermodynamic potential f, the set of variables of state x, and the vector u constitute the complete set of $2n+1$ variables, which completely define the given thermodynamic system.

The first thermodynamic potential $g=g(y)$ is a function of a new set of independent variables of state $y=(u_1, \ldots, u_m, x_{m+1}, \ldots, x_n)$, which is obtained by the Legendre transform from the fundamental thermodynamic potential $f(x_1, \ldots, x_n)$ changing $m \le n$ variables of state $(x_1, \ldots, x_m)$ with their conjugate variables $(u_1, \ldots, u_m)$. The set of unknown variables $x_1, \ldots, x_m$ is a solution of a system of m differential equations [19]:

$$\frac{\partial f}{\partial x_i} = u_i \qquad (i = 1, \ldots, m). \tag{5}$$

Solving this system of equations, we obtain m functions of the variables of state,

$$x_i = x_i(u_1,\ldots,u_m,x_{m+1},\ldots,x_n) \qquad (i=1,\ldots,m). \tag{6}$$

Substituting Eq. (6) into the fundamental thermodynamic potential f and using the Legendre transform, we obtain [19]

$$g = f - \sum_{i=1}^{m} \frac{\partial f}{\partial x_i} x_i = f - \sum_{i=1}^{m} u_i x_i. \tag{7}$$

This Legendre transform is always well defined when the fundamental thermodynamic potential $f(x_1, \ldots, x_n)$ is a convex function of the variables $(x_1, \ldots, x_m)$, i.e., the quadratic form $\sum_{i,j=1}^{m} a_{ij} d x_i d x_j$ is positive definite [19]. To obtain this, it is necessary and sufficient to satisfy the relations (4) for $s=m$ [18].

The first differential and the first partial derivatives of the first thermodynamic potential g can be written as

$$\begin{aligned} dg &= \sum_{i=1}^{n} v_i dy_i, \qquad v_i = \frac{\partial g}{\partial y_i}, \\ v_i &= \frac{\partial g}{\partial u_i} = -x_i \qquad (i=1,\ldots,m), \\ v_i &= \frac{\partial g}{\partial x_i} = u_i \qquad (i=m+1,\ldots,n). \end{aligned} \tag{8}$$

The second differential and the second partial derivatives of the first thermodynamic potential g are

$$d^2 g = \sum_{i=1}^{n}\sum_{j=1}^{n} b_{ij} dy_i dy_j, \quad b_{ij} = \frac{\partial^2 g}{\partial y_i \partial y_j}. \tag{9}$$

The symmetry conditions for the matrix elements, $b_{ij}=b_{ji}$, impose the following equalities

$$\begin{aligned} \frac{\partial x_j}{\partial u_i} &= \frac{\partial x_i}{\partial u_j} \qquad (i,j=1,\ldots,m), \\ \frac{\partial u_j}{\partial u_i} &= -\frac{\partial x_i}{\partial x_j} \qquad (i=1,\ldots,m, j=m+1,\ldots,n), \\ \frac{\partial u_j}{\partial x_i} &= \frac{\partial u_i}{\partial x_j} \qquad (i,j=m+1,\ldots,n). \end{aligned} \tag{10}$$

http://dx.doi.org/10.5772/60997

If the function $g(u_1, \ldots, u_m, x_{m+1}, \ldots, x_n)$ is convex (concave) on $s \leq n$ variables of state, then the quadratic form (Eq. (9)) in s variables is positive definite (negative definite). The quadratic form (Eq. (9)) in s variables for which $b_{ij}=b_{ji}$ is positive definite (negative definite) if [18]

$$b_{11}\xi > 0,\ \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} \xi^2 > 0,\ \ldots,\ \begin{vmatrix} b_{11} & b_{12} & \ldots & b_{1s} \\ b_{21} & b_{22} & \ldots & b_{2s} \\ \vdots & \vdots & \ddots & \vdots \\ b_{s1} & b_{s2} & \ldots & b_{ss} \end{vmatrix} \xi^s > 0 \tag{11}$$

for every nonzero vector y, where $\xi=1$ for the positive definite quadratic form and $\xi=-1$ for the negative definite quadratic form.

The Legendre transform (Eq. (7)) is involutive [19], i.e., if under the Legendre transformation f is taken to g, then the Legendre transform of g will again be f. The fundamental thermodynamic potential $f(x_1, \ldots, x_n)$ can be obtained from the first thermodynamic potential $g(u_1, \ldots, u_m, x_{m+1}, \ldots, x_n)$ by the Legendre back-transformation

$$f = g - \sum_{i=1}^{m} \frac{\partial g}{\partial u_i} u_i = g + \sum_{i=1}^{m} x_i u_i, \tag{12}$$

where m functions $u_i=u_i(x_1, \ldots, x_n)$, $i=1, \ldots, m$ are the solutions of the system of m differential equations

$$\frac{\partial g}{\partial u_i} = -x_i \quad (i = 1,\ldots,m). \tag{13}$$

This Legendre transform is well defined when the function $g(u_1, \ldots, u_m, x_{m+1}, \ldots, x_n)$ is a convex function of the variables $(u_1, \ldots, u_m)$, i.e., the quadratic form $\sum_{i,j=1}^{m} b_{ij} d u_i d u_j$ is positive definite [19]. To obtain this, it is necessary and sufficient to satisfy the relations (Eq. (11)) for $s=m$ [18].

The second thermodynamic potential $h=h(r)$ is obtained from the fundamental thermodynamic potential $f=f(x_1, \ldots, x_n)$ by expressing the variable x_k through the set of independent variables $r=(x_1, \ldots, x_{k-1}, f, x_{k+1}, \ldots, x_n)$:

$$h = x_k(x_1,\ldots,x_{k-1},f,x_{k+1},\ldots,x_n), \tag{14}$$

where, now, x_k is the second thermodynamic potential and f is a variable of state. The condition of independence of the variables of state r can be written as

$$\frac{\partial f}{\partial x_i}+\frac{\partial f}{\partial h}\frac{\partial h}{\partial x_i}=0. \tag{15}$$

Then the first differential and the first partial derivatives of the second thermodynamic potential h can be written as

$$dh=\sum_{i=1}^{n}w_i dr_i, \quad w_i=\frac{\partial h}{\partial r_i}, \tag{16}$$

$$\begin{aligned} w_i &= \frac{\partial x_k}{\partial f}=\frac{1}{u_k} \qquad (i=k), \\ w_i &= \frac{\partial x_k}{\partial x_i}=-\frac{u_i}{u_k} \quad (i=1,\ldots,n, i\neq k). \end{aligned} \tag{17}$$

The second differential and the second partial derivatives of the second thermodynamic potential h can be written as

$$d^2h=\sum_{i=1}^{n}\sum_{j=1}^{n}c_{ij}dr_i dr_j, \qquad c_{ij}=\frac{\partial^2 h}{\partial r_i \partial r_j}, \tag{18}$$

$$c_{ii}=\frac{\partial^2 x_k}{\partial f^2}=-\frac{1}{u_k^2}\frac{\partial u_k}{\partial f} \quad (i=k). \tag{19}$$

The symmetry conditions for the matrix elements, $c_{ij}=c_{ji}$, impose the following equalities

$$\begin{aligned} \frac{u_i}{u_k^2}\frac{\partial u_k}{\partial f}-\frac{1}{u_k}\frac{\partial u_i}{\partial f} &= -\frac{1}{u_k^2}\frac{\partial u_k}{\partial x_i} \qquad (i\neq k), \\ \frac{u_j}{u_k^2}\frac{\partial u_k}{\partial x_i}-\frac{1}{u_k}\frac{\partial u_j}{\partial x_i} &= \frac{u_i}{u_k^2}\frac{\partial u_k}{\partial x_j}-\frac{1}{u_k}\frac{\partial u_i}{\partial x_j} \qquad (i,j\neq k). \end{aligned} \tag{20}$$

2.2. Principle of additivity

In the equilibrium thermodynamics, all thermodynamic quantities belong to the class of homogeneous functions of zero and first order, which imposes the additional constraints on the thermodynamic system. The homogeneous function of k th order satisfies the relation [14, 15, 20]

http://dx.doi.org/10.5772/60997

$$f\left(\lambda x_1,\ldots,\lambda x_m,x_{m+1},\ldots,x_n\right)=\lambda^k f\left(x_1,\ldots,x_m,x_{m+1},\ldots,x_n\right) \tag{21}$$

and the Euler theorem[1]

$$\sum_{i=1}^{m}\frac{\partial f}{\partial x_i}x_i=kf, \tag{22}$$

where $(x_1, \ldots, x_m)$ are extensive variables and $(x_{m+1}, \ldots, x_n)$ are intensive variables. Note that the function f is extensive if $k=1$, and it is intensive if $k=0$.

Let us divide the system into two subsystems: system(1+2) = system(1) + system(2).

Then m -extensive and $n-m$ -intensive variables of state satisfy the additivity relations [6, 15]

$$\begin{aligned} x_i^{1+2}&=x_i^1+x_i^2 \qquad \left(i=1,\ldots,m\right),\\ x_i^{1+2}&=x_i^1=x_i^2 \qquad \left(i=m+1,\ldots,n\right). \end{aligned} \tag{23}$$

The homogeneous function of the first degree ($k=1$), which is extensive, is an additive function of the first order [15]

$$f^{1+2}\left(x_1^{1+2},\ldots,x_n^{1+2}\right)=f^1\left(x_1^1,\ldots,x_n^1\right)+f^2\left(x_1^2,\ldots,x_n^2\right) \tag{24}$$

and the homogeneous function of the zero degree ($k=0$), which is intensive, is an additive function of zero order [15]

$$f^{1+2}\left(x_1^{1+2},\ldots,x_n^{1+2}\right)=f^1\left(x_1^1,\ldots,x_n^1\right)=f^2\left(x_1^2,\ldots,x_n^2\right). \tag{25}$$

Note that the zero law of thermodynamics is expressed by Eqs. (21) and (25) when the temperature T is a function or the second equation of Eq. (23) when temperature T is a variable of state.

3. Equilibrium statistical mechanics

In comparison with the equilibrium thermodynamics, the system in the equilibrium statistical mechanics is described by two additional elements: the microstates of the system and the

1 In this subsection, the symbol f denotes any function not only the fundamental thermodynamic potential.

probabilities of these microstates. As in the equilibrium thermodynamics, the macrostates of the system are fixed by the set of independent variables of state. The thermodynamic potential is a universal function that depends not only on the macroscopic state variables of the system but also on the microstates of the system and their probabilities. The extensive thermodynamic quantities are calculated as averages over the ensemble of microstates. However, the intensive thermodynamic quantities are defined in terms of the first derivatives of the thermodynamic potential with respect to the extensive variables of state.

Let us formulate the main statements of the equilibrium statistical mechanics. Let the thermodynamic potential be a function $Y = Y(p_1, \ldots, p_W; X^1, \ldots, X^n)$ of W -independent variables $(p_1, \ldots, p_W)$ and n variables of state $(X^1, \ldots, X^n)$. All arguments of the function Y are independent.[2]

The first thermodynamic potential $Y = g(p_1, \ldots, p_W; u^1, \ldots, u^m, x^{m+1}, \ldots, x^n)$ is a function of m intensive variables of state $X^j = u^j$ $(j = 1, \ldots, m)$ conjugated to the variables $(x^1, \ldots, x^m)$ and $n - m$ extensive variables of state $X^j = x^j$ $(j = m + 1, \ldots, n)$. The first thermodynamic potential Y is related to the fundamental thermodynamic potential $f = f(p_1, \ldots, p_W; x^1, \ldots, x^n)$ by the Legendre transform (7) [19]

$$Y = f - \sum_{j=1}^{m} u^j x^j, \qquad u^j = \frac{\partial f}{\partial x^j}. \tag{26}$$

Here and in the following, the first thermodynamic potential will be considered only for the statistical ensembles for which $x^1 = S$, $X^1 = u^1 = T$, and $f = E$, where S is the entropy, T is the temperature, and E is the energy.

The second thermodynamic potential $Y = h = x^k(p_1, \ldots, p_W; x^1, \ldots, x^{k-1}, f, x^{k+1}, \ldots, x^n)$ is a function of $n - 1$ variables of state $X^j = x^j$ $(j = 1, \ldots, n, j \neq k)$ and one variable $X^k = f$ for $1 \leq k \leq n$. In the following, the second thermodynamic potential will be associated only with the microcanonical ensemble $(k = 1)$ for which $Y = x^1 = S$ and $X^1 = f = E$.

Let Y_i and $x_i^1, \ldots, x_i^n$ be the values of the dynamical extensive variables Y and $x^1, \ldots, x^n$, respectively, in the i th microscopic state of the system. Moreover, let us impose an additional constraint on the variables $(p_1, \ldots, p_W)$ [18],

$$\varphi\left(p_1, \ldots, p_W; X^1, \ldots, X^n\right) = \sum_i \delta_{X^{m+1}, X_i^{m+1}} \ldots \delta_{X^n, X_i^n} p_i - 1 = 0, \tag{27}$$

where $\delta_{x,x'}$ is the Kronecker delta for the integer x, x' and the Dirac delta function for the real x, x'. In Eq. (27), the variables $X_i^j = x_i^j$ $(j = m + 1, \ldots, n)$ are for the first thermodynamic potential,

2 In this section, the thermodynamic quantities are numbered by the index at the top. The index at the bottom of the variable denotes the microstate of the system.

and $m=0$, $X^1=f=E$, $X_i^1=f_i=E_i$, and $X_i^j=x_i^j$ ($j=2, \ldots, n$) are for the second thermodynamic potential.

The ensemble averages for the extensive dynamical variables A can be written as

$$A\left(p_1,\ldots,p_W;X^1,\ldots,X^n\right)=\sum_i \delta_{X^{m+1},X_i^{m+1}}\ldots\delta_{X^n,X_i^n}p_iA_i, \tag{28}$$

where A_i is the value of the variable A in the i th microscopic state of the system.

The first and the second thermodynamic potentials, which are the extensive functions of the variables of state, can also be written as (28)

$$Y(p_1,\ldots,p_W;X^1,\ldots,X^n)=\sum_i \delta_{X^{m+1},X_i^{m+1}}\ldots\delta_{X^n,X_i^n}p_iY_i, \tag{29}$$

$$Y_i=f_i-\sum_{j=1}^{m}u^jx_i^j \qquad \text{for } Y=g, \tag{30}$$

$$Y_i=x_i^1=S_i \qquad \text{for } Y=x^1=S, \tag{31}$$

where S_i and f_i are the values of the entropy S and the fundamental thermodynamic potential f, respectively, in the i th microstate of the system, which are both determined by Eq. (28).

In the equilibrium statistical mechanics, the unknown probabilities of microstates $\{p_i\}$ are found from the second part of the second law of thermodynamics, i.e., from the constrained extremum of the thermodynamic potential (Eq. (29)) as a function of the variables ($p_1, \ldots, p_W$) under the condition that the variables ($p_1, \ldots, p_W$) satisfy Eq. (27). Moreover, it is supposed that the value of the entropy in the i th microstate of the system is a function of the probability p_i of this microstate, i.e., $x_i^1=S_i=S_i(p_i)$. Then to determine the unknown probabilities $\{p_i\}$ at which the function Y attains the constrained local extrema, the method of Lagrange multipliers [18] can be used

$$\Phi\left(p_1,\ldots,p_W;X\right)=Y\left(p_1,\ldots,p_W;X\right)-\lambda\varphi\left(p_1,\ldots,p_W;X\right), \tag{32}$$

$$\frac{\partial\Phi(p_1,\ldots,p_W;X)}{\partial p_i}=0 \qquad (i=1,\ldots,W), \tag{33}$$

where λ is an arbitrary constant and the vector $X=(X^1, \ldots, X^n)$. Substituting Eqs. (27) and (29) into Eq. (32), we obtain

$$\Upsilon_i + p_i \frac{\partial \Upsilon_i}{\partial p_i} - \lambda = 0 \quad \left(i = 1,\ldots,W\right). \tag{34}$$

Substituting Eq. (30) into Eq. (34) and using Eq. (27), we obtain the probabilities related to the first thermodynamic potential

$$p_i = \psi\left(\frac{1}{u^1}\left(\Lambda - f_i + \sum_{j=2}^{m} u^j x_i^j\right)\right), \tag{35}$$

$$\sum_i \delta_{x^{m+1},x_i^{m+1}} \ldots \delta_{x^n,x_i^n} \psi\left(\frac{1}{u^1}\left(\Lambda - f_i + \sum_{j=2}^{m} u^j x_i^j\right)\right) = 1, \tag{36}$$

where $\Lambda \equiv \phi(\lambda) = \Lambda(u^1, \ldots, u^m, x^{m+1}, \ldots, x^n)$ is the solution of Eq. (36) and $\psi(x)$ is a function related to the given function $x_i^1 = S_i(p_i)$.

Substituting Eq. (31) into Eq. (34) and using Eq. (27), we obtain the probabilities related to the second thermodynamic potential

$$p_i = \frac{1}{W\left(f, x^2, \ldots, x^n\right)}, \tag{37}$$

$$W\left(f, x^2, \ldots, x^n\right) = \sum_i \delta_{f,f_i} \delta_{x^2,x_i^2} \ldots \delta_{x^n,x_i^n}, \tag{38}$$

where $p_i = \psi(\lambda)$ is a constant the same for all microstates of the system. Note that in these derivations, the conditions $\partial f_i / \partial p_i = 0$, $\partial u^j / \partial p_i = 0$ ($j = 1, \ldots, m$), and $\partial x_i^j / \partial p_i = 0$ ($j = 2, \ldots, m$) were used.

Let us consider the first thermodynamic potential. Substituting Eq. (35) into Eq. (26) and using Eq. (36), we obtain the expression for the first thermodynamic potential as

$$\begin{aligned} \Upsilon\left(u^1, \ldots, u^m, x^{m+1}, \ldots, x^n\right) &= f\left(u^1, \ldots, u^m, x^{m+1}, \ldots, x^n\right) \\ &\quad - \sum_{j=1}^{m} u^j x^j \left(u^1, \ldots, u^m, x^{m+1}, \ldots, x^n\right). \end{aligned} \tag{39}$$

Then the partial derivatives of the first thermodynamic potential (Eq. (39)) with respect to the variables of state can be written as

http://dx.doi.org/10.5772/60997

$$x^k = -\frac{\partial Y}{\partial u^k} = \sum_i \delta_{x^{m+1},x_i^{m+1}} \cdots \delta_{x^n,x_i^n} p_i x_i^k \qquad \left(k = 1,\ldots,m\right), \tag{40}$$

$$\begin{aligned} u^k = \frac{\partial Y}{\partial x^k} &= \sum_i \delta_{x^{m+1},x_i^{m+1}} \cdots \delta_{x^n,x_i^n} p_i \frac{\partial f_i}{\partial x^k} \\ &+ \sum_i \delta_{x^{m+1},x_i^{m+1}} \cdots \delta_{x^n,x_i^n} \left(\frac{\partial \delta_{x^k,x_i^k}}{\partial x^k}\right) p_i Y_i \qquad \left(k = m+1,\ldots,n\right). \end{aligned} \tag{41}$$

Here we used the conditions $\partial f_i / \partial u^k = 0$, $\partial x_i^j / \partial u^k = 0$ ($j = 2, \ldots, n$) and Eqs. (34) and (36).

The fundamental thermodynamic potential can be written as

$$f = Y - \sum_{j=1}^{m} u^j \frac{\partial Y}{\partial u^j} = \sum_i \delta_{x^{m+1},x_i^{m+1}} \cdots \delta_{x^n,x_i^n} p_i f_i. \tag{42}$$

Let us consider the second thermodynamic potential. Substituting Eqs. (37), (38), and (31) into Eq. (29), we obtain the expression for the second thermodynamic potential

$$Y\left(f, x^2, \ldots, x^n\right) = S_i\left(p_i\right), \tag{43}$$

where p_i is determined from Eq. (37) and $Y = S$. The partial derivatives (Eq. (17)) of the second thermodynamic potential (Eq. (43)) with respect to the variables of state can be written as

$$\frac{1}{u^1} = \frac{\partial Y}{\partial f} = -\gamma \frac{\partial \ln W}{\partial f}, \qquad \gamma \equiv p_i \frac{\partial S_i\left(p_i\right)}{\partial p_i}, \tag{44}$$

$$\frac{u^j}{u^1} = -\frac{\partial Y}{\partial x^j} = \gamma \frac{\partial \ln W}{\partial x^j} - \left.\frac{\partial S_i}{\partial x^j}\right|_{p_i = const} \qquad \left(j = 2,\ldots,n\right), \tag{45}$$

where W is determined from Eq. (38).

Finally, it should be mentioned that the equilibrium statistical mechanics is thermodynamically self-consistent if the statistical variables (x^1, …, x^n), the potentials (f, g, …), and the variables (u^1, …, u^n) are homogeneous variables of the first- or zero-order satisfying Eqs. (21)-(25).

4. Tsallis statistical mechanics

The Tsallis statistical mechanics is based on the generalized entropy which is a function of the entropic parameter q and probing probabilities p_i [3, 4]:

$$S = \sum_i p_i S_i, \qquad S_i = k_B z\left(1 - p_i^{1/z}\right), \tag{46}$$

where $z = 1/(q-1)$, k_B is the Boltzmann constant, and $q \in \mathbb{R}$ is a real parameter, $0 < q < \infty$. In the limit $q \to 1$ ($z \to \pm\infty$), the entropy (Eq. (46)) recovers the usual Boltzmann-Gibbs entropy $S = \sum_i p_i S_i$, where $S_i = -k_B \ln p_i$ [3]. Note that throughout the work, we use the system of natural units $\hbar = c = k_B = 1$.

4.1. Canonical ensemble

The thermodynamic potential of the canonical ensemble, the Helmholtz free energy, is the first thermodynamic potential $g = F$, which is a function of the variables of state $u^1 = T$, $x^2 = V$, $x^3 = N$, and $x^4 = z$. It is obtained from the fundamental thermodynamic potential $f = E$ (the energy) by the Legendre transform (Eq. (7)), exchanging the variable of state $x^1 = S$ of the fundamental thermodynamic potential with its conjugate variable $u^1 = T$. In the canonical ensemble, the first partial derivatives (Eq. (1)) of the fundamental thermodynamic potential are defined as $u^2 = -p$, $u^3 = \mu$, and $u^4 = -\Xi$. The entropy (Eq. (46)) for the Tsallis and Boltzmann-Gibbs statistics in the canonical ensemble can be rewritten as

$$S = \sum_i \delta_{V,V_i} \delta_{N,N_i} \delta_{z,z_i} p_i S_i, \tag{47}$$

$$S_i = z_i(1 - p_i^{1/z_i}) \qquad \text{for } |z| < \infty, \tag{48}$$

$$S_i = -\ln p_i \qquad \text{for } |z| = \infty. \tag{49}$$

The first thermodynamic potential (Eqs. (26) and (29)), $Y = F$, for the Tsallis and Boltzmann-Gibbs statistics can be rewritten as

$$F = E - TS = \sum_i \delta_{V,V_i} \delta_{N,N_i} \delta_{z,z_i} p_i F_i, \qquad F_i \equiv E_i - TS_i, \tag{50}$$

$$F_i = E_i - Tz_i\left(1 - p_i^{1/z_i}\right) \qquad \text{for } |z| < \infty, \tag{51}$$

http://dx.doi.org/10.5772/60997

$$F_i = E_i + T\ln p_i \qquad \text{for } |z| = \infty. \tag{52}$$

Here the constraint (Eq. (27)) in the canonical ensemble is in the form

$$\varphi = \sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i}p_i - 1 = 0. \tag{53}$$

Applying the method of Lagrange multipliers (Eqs. (32)-(34)) with the Lagrange function $\Phi = F - \lambda\varphi$ to Eqs. (50)-(53), we can write down Eqs. (34) and (35) for the Tsallis and Boltzmann-Gibbs statistics immediately as

$$F_i + p_i\frac{\partial F_i}{\partial p_i} - \lambda = 0 \tag{54}$$

and [7]

$$p_i = \left[1 + \frac{1}{z_i + 1}\frac{\Lambda - E_i}{T}\right]^{z_i} \qquad \text{for } |z| < \infty, \tag{55}$$

$$p_i = e^{\frac{\Lambda - E_i}{T}} \qquad \text{for } |z| = \infty, \tag{56}$$

where $\Lambda \equiv \lambda - T$ and $\partial E_i / \partial p_i = 0$. Then the constraint (Eq. (53)) for the probabilities (Eqs. (55) and (56)) of the Tsallis and Boltzmann-Gibbs statistics can be written as [7]

$$\sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i}\left[1 + \frac{1}{z_i + 1}\frac{\Lambda - E_i}{T}\right]^{z_i} = 1 \quad \text{for } |z| < \infty, \tag{57}$$

$$\sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i}e^{\frac{\Lambda - E_i}{T}} = 1 \qquad \text{for } |z| = \infty, \tag{58}$$

where $\Lambda = \Lambda(T, V, N, z)$ is the solution of Eq. (57) for the Tsallis statistics and $\Lambda = -T\ln Z_G$ is the solution of Eq. (58) for the Boltzmann-Gibbs statistics, where $Z_G = \sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i}e^{-E_i/T}$ is the partition function. Substitution of the probabilities given in Eqs. (55) and (56) into Eqs. (50)-(53) gives the Helmholtz free energy [7]

$$F = \frac{z}{z+1}\left(\Lambda + \frac{E}{z}\right) \qquad \text{for } |z| < \infty, \tag{59}$$

$$F = \Lambda = -T \ln Z_G \qquad \text{for } |z| = \infty, \tag{60}$$

where E is the energy (Eq. (42)), which can be written in terms of the canonical ensemble as

$$E = F - T\frac{\partial F}{\partial T} = \sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i} p_i E_i. \tag{61}$$

Making use of Eqs. (40), (50), and (54), we can write the entropy of the system as

$$S = -\frac{\partial F}{\partial T} = \sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i} p_i S_i. \tag{62}$$

Here we have used the conditions that the derivative of the constraint (Eq. (53)) with respect to T is zero, $\partial E_i / \partial T = 0$, $\partial E_i / \partial p_i = 0$, and $\partial T / \partial p_i = 0$. Substituting Eqs. (48), (49), (55), and (56) into Eq. (62) and using Eqs. (57) and (58), we obtain [7]

$$S = -\frac{z}{z+1}\frac{\Lambda - E}{T} \qquad \text{for } |z| < \infty, \tag{63}$$

$$S = -\frac{\Lambda - E}{T} \qquad \text{for } |z| = \infty. \tag{64}$$

Using Eqs. (41), (50), and (54), we obtain the pressure, $u^2 = -p$, and the chemical potential, $u^3 = \mu$:

$$-p = \frac{\partial F}{\partial V} = \sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i} p_i \frac{\partial E_i}{\partial V} + \sum_i \delta_{N,N_i}\delta_{z,z_i}\left(\frac{\partial \delta_{V,V_i}}{\partial V}\right) p_i F_i, \tag{65}$$

$$\mu = \frac{\partial F}{\partial N} = \sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i} p_i \frac{\partial E_i}{\partial N} + \sum_i \delta_{V,V_i}\delta_{z,z_i}\left(\frac{\partial \delta_{N,N_i}}{\partial N}\right) p_i F_i. \tag{66}$$

Here we have used the conditions that the derivatives of the constraint (Eq. (53)) with respect to the variables of state N and V are zero, $\partial E_i / \partial p_i = 0$ and $\partial T / \partial p_i = 0$.

http://dx.doi.org/10.5772/60997

Substituting Eqs. (50) and(54) into Eq. (41), we obtain the variable Ξ :

$$-\Xi = \frac{\partial F}{\partial z} = -T\sum_i \delta_{V,V_i}\delta_{N,N_i}\delta_{z,z_i} p_i\left[1 - p_i^{1/z_i}\left(1 - \ln p_i^{1/z_i}\right)\right] + \sum_i \delta_{V,V_i}\delta_{N,N_i}\left(\frac{\partial \delta_{z,z_i}}{\partial z}\right) p_i F_i \qquad \text{for } |z| < \infty, \tag{67}$$

$$-\Xi = \frac{\partial F}{\partial z} = 0 \qquad \text{for } |z| = \infty, \tag{68}$$

where we have used the conditions that the derivative of the constraint (53) with respect to z is zero, $\partial E_i / \partial z = 0$, $\partial E_i / \partial p_i = 0$, and $\partial T / \partial p_i = 0$.

Thus, from the results given in Eqs. (62) and (65)-(67), we see that the differential of the thermodynamic potential (Eq. (50)) satisfies [7, 15]

$$dF = -SdT - pdV + \mu dN - \Xi dz. \tag{69}$$

Using Eqs. (50) and (69), we obtain the fundamental equation of thermodynamics [7, 14, 15]

$$TdS = dE + pdV - \mu dN + \Xi dz. \tag{70}$$

To prove the homogeneity properties of the thermodynamic quantities and the Euler theorem for the Tsallis statistics in the canonical ensemble, we will consider, as an example, the exact analytical results for the nonrelativistic ideal gas.

4.1.1. Nonrelativistic ideal gas: canonical ensemble

Let us investigate the nonrelativistic ideal gas of identical particles governed by the classical Maxwell-Boltzmann statistics in the framework of the Tsallis and Boltzmann-Gibbs statistical mechanics.

It is convenient to obtain the exact results for the ideal gas in the Tsallis statistics by means of the integral representation for the Gamma function (see [9] and reference therein):

$$x^{-y} = \frac{1}{\Gamma(y)}\int_0^\infty dt t^{y-1} e^{-tx}, \qquad \mathrm{Re}\, x > 0,\ \mathrm{Re}\, y > 0, \tag{71}$$

$$x^{y-1} = \Gamma(y)\frac{i}{2\pi}\oint_C dt\left(-t\right)^{-y} e^{-tx}, \qquad \mathrm{Re}\, x > 0,\ |y| < \infty. \tag{72}$$

Thus, solving Eqs. (57) and (58) for the ideal gas in the canonical ensemble, the norm function Λ is [7]

$$1+\frac{1}{z+1}\frac{\Lambda}{T}=\left[Z_G\frac{\Gamma\left(-z-3N/2\right)}{\left(-z-1\right)^{-3N/2}\Gamma\left(-z\right)}\right]^{-\frac{1}{z+3N/2}} \quad \text{for } z<-1, \tag{73}$$

$$1+\frac{1}{z+1}\frac{\Lambda}{T}=\left[Z_G\frac{\left(z+1\right)^{3N/2}\Gamma\left(z+1\right)}{\Gamma\left(z+1+3N/2\right)}\right]^{-\frac{1}{z+3N/2}} \quad \text{for } z>0, \tag{74}$$

$$Z_G=\frac{\left(gV\right)^N}{N!}\left(\frac{mT}{2\pi}\right)^{\frac{3}{2}N} \tag{75}$$

and $\Lambda=-T\ln Z_G$ for $|z|=\infty$. Here m is the particle mass, and Eq. (73) is restricted by the condition $-z-3N/2>0$.

The energy (Eq. (61)) and the thermodynamic potentials (Eqs. (59) and (60)) for the ideal gas in the canonical ensemble for the Tsallis and Boltzmann-Gibbs statistics can be written as [7]

$$E=\frac{3}{2}TN\eta,\quad \eta=\left(1+\frac{1}{z+1}\frac{\Lambda}{T}\right)\left(1+\frac{1}{z+1}\frac{3}{2}N\right)^{-1} \quad \text{for } |z|<\infty, \tag{76}$$

$$F=-T\left[z-\left(z+\frac{3}{2}N\right)\eta\right] \quad \text{for } |z|<\infty \tag{77}$$

and $E=3TN/2$ and $F=\Lambda=-T\ln Z_G$ for $|z|=\infty$.

The entropies (Eqs. (63) and (64)) and the pressure (Eq. (65)) for the ideal gas in the canonical ensemble for the Tsallis and Boltzmann-Gibbs statistics can be written as [7]

$$S=z\left(1-\eta\right) \quad \text{for } |z|<\infty, \tag{78}$$

$$p=\frac{N}{V}T\,\eta=\frac{2}{3}\frac{E}{V} \quad \text{for } |z|<\infty \tag{79}$$

and $S=\ln Z_G+3N/2$, $p=NT/V$ for $|z|=\infty$.

http://dx.doi.org/10.5772/60997

The chemical potential (Eq. (66)) and the variable (Eqs. (67) and (68)) for the ideal gas in the canonical ensemble for the Tsallis and Boltzmann-Gibbs statistics become [7]

$$\begin{aligned}\mu &= -T\eta\left[\ln\left(gV\left(\frac{mT}{2\pi}\gamma_1(z+1)\left(1+\frac{1}{z+1}\frac{\Lambda}{T}\right)\right)^{3/2}\right)-\frac{3}{2}\frac{1}{z+1+3N/2}\right]\\ &+T\eta\left[\psi(N+1)+\frac{3}{2}\psi\left(a_1+\gamma_1\frac{3}{2}N\right)\right] \qquad \text{for } |z|<\infty,\end{aligned} \tag{80}$$

$$\begin{aligned}\Xi &= T\left[1-\eta\left(1+\frac{z}{(z+1)^2}\frac{3}{2}N\right)\left(1+\frac{1}{z+1}\frac{3}{2}N\right)^{-1}\right]\\ &+T\eta\left[\ln\left(1+\frac{1}{z+1}\frac{\Lambda}{T}\right)+\psi(a_1)-\psi\left(a_1+\gamma_1\frac{3}{2}N\right)\right] \qquad \text{for } |z|<\infty\end{aligned} \tag{81}$$

and $\mu=-T[\ln(gV(mT/2\pi)^{3/2})-\psi(N+1)]$, $\Xi=0$ for $|z|=\infty$, where $\psi(y)$ is the psi-function, $a_1=-z$, $\gamma_1=-1$ for $z<-1$ and $a_1=z+1$, $\gamma_1=1$ for $z>0$.

4.1.2. Nonrelativistic ideal gas in the thermodynamic limit: canonical ensemble

Let us try to express the thermodynamic quantities of the nonrelativistic ideal gas directly in terms of the thermodynamic limit when the entropic parameter z is considered as an extensive variable of state

$$V\to\infty,\ N\to\infty,\ |z|\to\infty,\ v=\frac{V}{N}=const,\ \tilde{z}=\frac{z}{N}=const. \tag{82}$$

Note first that the canonical partition function (Eq. (75)) for the nonrelativistic ideal gas for the Boltzmann-Gibbs statistics can be rewritten as

$$Z_G=\tilde{Z}_G{}^N,\ \ \tilde{Z}_G\equiv gve\left(\frac{mT}{2\pi}\right)^{3/2}. \tag{83}$$

The norm functions (Eqs. (73) and (74)) for the ideal gas in the thermodynamic limit in the Tsallis and Boltzmann-Gibbs statistics can be rewritten as [7]

$$\Lambda=-TN\left[\tilde{z}-\left(\tilde{z}+\frac{3}{2}\right)\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\right] \quad \text{for } |\tilde{z}|<\infty, \tag{84}$$

$$\Lambda = -TN\ln\tilde{Z}_G \qquad \text{for } |\tilde{z}| = \infty, \tag{85}$$

where Eq. (84) is restricted by the conditions $\tilde{z} < -3/2$ and $\tilde{z} > 0$.

In the thermodynamic limit (Eq. (82)), the energy of the system (Eq. (76)) and the thermodynamic potential (Eq. (77)) for the ideal gas in the canonical ensemble for the Tsallis and Boltzmann-Gibbs statistics become [7]

$$E = \frac{3}{2}TN\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}} \qquad \text{for } |\tilde{z}| < \infty, \tag{86}$$

$$E = \frac{3}{2}TN \qquad \text{for } |\tilde{z}| = \infty \tag{87}$$

and [7]

$$F = \Lambda = -TN\left[\tilde{z} - \left(\tilde{z}+\frac{3}{2}\right)\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\right] \quad \text{for } |\tilde{z}| < \infty, \tag{88}$$

$$F = \Lambda = -TN\ln\tilde{Z}_G \qquad \text{for } |\tilde{z}| = \infty, \tag{89}$$

respectively. The entropy (78) and the pressure (79) for the ideal gas in the Tsallis and Boltzmann-Gibbs statistics in the thermodynamic limit can be written as [7]

$$S = N\tilde{z}\left[1 - \left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\right] \qquad \text{for } |\tilde{z}| < \infty, \tag{90}$$

$$S = N\left(\ln\tilde{Z}_G + 3/2\right) \qquad \text{for } |\tilde{z}| = \infty \tag{91}$$

and [7]

$$p = \frac{T}{v}\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}} = \frac{2}{3}\frac{\varepsilon}{v} \qquad \text{for } |\tilde{z}| < \infty, \tag{92}$$

$$p = \frac{T}{v} = \frac{2}{3}\frac{\varepsilon}{v} \qquad \text{for } |\tilde{z}| = \infty, \tag{93}$$

http://dx.doi.org/10.5772/60997

where $\varepsilon = E/N$ is the specific energy given in Eqs. (86) and (87).

In the thermodynamic limit (82), the chemical potential (80) and the variable (81) for the ideal gas in the canonical ensemble for the Tsallis and Boltzmann-Gibbs statistics are [7]

$$\mu = T\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\left[\frac{5}{2}+\tilde{z}\ln\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\right] \quad \text{for } |\tilde{z}|<\infty, \tag{94}$$

$$\mu = T\left(1-\ln\tilde{Z}_G\right) \qquad \text{for } |\tilde{z}|=\infty \tag{95}$$

and [7]

$$\Xi = T\left[1-\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\left(1-\ln\left(\tilde{Z}_G e^{3/2}\right)^{-\frac{1}{\tilde{z}+\frac{3}{2}}}\right)\right] \quad \text{for } |\tilde{z}|<\infty, \tag{96}$$

$$\Xi = 0 \qquad \text{for } |\tilde{z}|=\infty. \tag{97}$$

Thus, from the results for the Tsallis statistics given in Eqs. (86), (90), (92), (94), and (96), we see that the Euler theorem (Eq. (22)) is satisfied [7]

$$TS = E + pV - \mu N + \Xi z. \tag{98}$$

Moreover, the thermodynamic quantities (86), (88), (90), (92), (94) and (96) satisfy the relation for the thermodynamic potential

$$F = E - TS = -pV + \mu N - \Xi z. \tag{99}$$

Next we shall verify that, when the entropic parameter z is an extensive variable of state in the thermodynamic limit, the ideal gas is in accordance with the principle of additivity. Suppose that the system is divided into two subsystems (1 and 2). Then the extensive variables of state of the canonical ensemble are additive

$$V^{1+2} = V^1 + V^2, \quad N^{1+2} = N^1 + N^2, \quad z^{1+2} = z^1 + z^2. \tag{100}$$

However, the temperature and the specific variables of state (Eq. (82)) are the same in each subsystem

$$T^{1+2} = T^1 = T^2, \quad v^{1+2} = v^1 = v^2, \quad \tilde{z}^{1+2} = \tilde{z}^1 = \tilde{z}^2. \tag{101}$$

Considering Eqs. (83), (100), and (101), we can verify that the Tsallis thermodynamic potential (Eq. (88)) and the entropy (Eq. (90)) of the canonical ensemble are homogeneous functions of the first order, i.e., $F(T, V, N, z)/N = F(T, v, \tilde{z})$ and $S(T, V, N, z)/N = S(T, v, \tilde{z})$, respectively, and they are additive (extensive)

$$F^{1+2}\left(T^{1+2}, V^{1+2}, N^{1+2}, z^{1+2}\right) = F^1\left(T^1, V^1, N^1, z^1\right) + F^2\left(T^2, V^2, N^2, z^2\right), \tag{102}$$

$$S^{1+2}\left(T^{1+2}, V^{1+2}, N^{1+2}, z^{1+2}\right) = S^1\left(T^1, V^1, N^1, z^1\right) + S^2\left(T^2, V^2, N^2, z^2\right). \tag{103}$$

The Tsallis pressure (Eq. (92)), the chemical potential (Eq. (94)), and the variable (Eq. (96)) are the homogeneous functions of the zero order, i.e., $p(T, V, N, z) = p(T, v, \tilde{z})$, $\mu(T, V, N, z) = \mu(T, v, \tilde{z})$, and $\Xi(T, V, N, z) = \Xi(T, v, \tilde{z})$, respectively, and they are the same in each subsystem (intensive)

$$p^{1+2}\left(T^{1+2}, V^{1+2}, N^{1+2}, z^{1+2}\right) = p^1\left(T^1, V^1, N^1, z^1\right) = p^2\left(T^2, V^2, N^2, z^2\right), \tag{104}$$

$$\mu^{1+2}\left(T^{1+2}, V^{1+2}, N^{1+2}, z^{1+2}\right) = \mu^1\left(T^1, V^1, N^1, z^1\right) = \mu^2\left(T^2, V^2, N^2, z^2\right), \tag{105}$$

$$\Xi^{1+2}\left(T^{1+2}, V^{1+2}, N^{1+2}, z^{1+2}\right) = \Xi^1\left(T^1, V^1, N^1, z^1\right) = \Xi^2\left(T^2, V^2, N^2, z^2\right). \tag{106}$$

Thus, the principle of additivity (Eqs. (21), (24), and (25)) is totally satisfied by the Tsallis statistics. Equations (101) and (103) prove the zero law of thermodynamics for the canonical ensemble.

4.2. Microcanonical ensemble

The thermodynamic potential of the microcanonical ensemble, the entropy, is the second thermodynamic potential $h = x^1 = S$ defined in Eq. (14), which is a function of the variables of state $f = E$, $x^2 = V$, $x^3 = N$ and $x^4 = z$. It is obtained from the fundamental thermodynamic potential f by exchanging the variable of state x^1 with variable f. In the microcanonical ensemble, the first partial derivatives of the fundamental thermodynamic potential (1) are defined as $u^1 = T$, $u^2 = -p$, $u^3 = \mu$, and $u^4 = -\Xi$.

The entropy S for the Tsallis and Boltzmann-Gibbs statistics in the microcanonical ensemble can be written as

http://dx.doi.org/10.5772/60997

$$S = \sum_i \delta_{E,E_i} \delta_{V,V_i} \delta_{N,N_i} \delta_{z,z_i} p_i S_i, \tag{107}$$

where S_i is defined in Eqs. (48) and (49). The set of probabilities $\{p_i\}$ is constrained by Eq. (27):

$$\varphi = \sum_i \delta_{E,E_i} \delta_{V,V_i} \delta_{N,N_i} \delta_{z,z_i} p_i - 1 = 0. \tag{108}$$

Applying the method of Lagrange multipliers (Eqs. (32)-(34)) with the Lagrange function $\Phi = S - \lambda\varphi$ to Eqs. (107), (108), (48), and (49), we can write down Eqs. (34), (37), and (38) for the Tsallis and Boltzmann-Gibbs statistics immediately as [6]

$$S_i + p_i \frac{\partial S_i}{\partial p_i} - \lambda = 0, \tag{109}$$

$$p_i = \frac{1}{W}, \tag{110}$$

$$W = \sum_i \delta_{E,E_i} \delta_{V,V_i} \delta_{N,N_i} \delta_{z,z_i}, \tag{111}$$

where $W = W(E, V, N)$ is the statistical weight for the Tsallis and Boltzmann-Gibbs statistics and $z_i = z$ for all microstates. Substituting Eqs. (110) and (111) into Eqs. (107), (48), and (49) and using Eq. (108), we can express the second thermodynamic potential (Eq. (43)) as [6]

$$S = z\left(1 - W^{-1/z}\right) \qquad \text{for } |z| < \infty, \tag{112}$$

$$S = \ln W \qquad \text{for } |z| = \infty. \tag{113}$$

Then the first derivative (Eq. (44)) of the thermodynamic potential S with respect to the variable of state E, i.e., the temperature T, can be rewritten as [6]

$$\frac{1}{T} = \frac{\partial S}{\partial E} = W^{-1/z} \frac{\partial \ln W}{\partial E} \qquad \text{for } |z| < \infty, \tag{114}$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial \ln W}{\partial E} \qquad \text{for } |z| = \infty. \tag{115}$$

The first derivative (Eq. (45)) of the thermodynamic potential S with respect to the variable of state V, i.e., the pressure p, becomes [6]

$$p = T\frac{\partial S}{\partial V} = TW^{-1/z}\frac{\partial \ln W}{\partial V} \qquad \text{for } |z| < \infty, \tag{116}$$

$$p = T\frac{\partial S}{\partial V} = T\frac{\partial \ln W}{\partial V} \qquad \text{for } |z| = \infty. \tag{117}$$

The first derivative (Eq. (45)) of the thermodynamic potential S with respect to the variable of state N, i.e., the chemical potential μ, is [6]

$$\mu = -T\frac{\partial S}{\partial N} = -TW^{-1/z}\frac{\partial \ln W}{\partial N} \qquad \text{for } |z| < \infty, \tag{118}$$

$$\mu = -T\frac{\partial S}{\partial N} = -T\frac{\partial \ln W}{\partial N} \qquad \text{for } |z| = \infty. \tag{119}$$

The first derivative (Eq. (45)) of the thermodynamic potential S with respect to the variable of state z, i.e., the variable Ξ, can be rewritten as [6]

$$\Xi = T\frac{\partial S}{\partial z} = T\left[1 - W^{-1/z}\left(1 - \ln W^{-1/z}\right)\right] \qquad \text{for } |z| < \infty, \tag{120}$$

$$\Xi = 0 \qquad \text{for } |z| = \infty, \tag{121}$$

where $\partial W/\partial z = 0$. Then the differential of the thermodynamic potential (107) satisfies the fundamental equation of thermodynamics (70).

4.2.1. Nonrelativistic ideal gas: microcanonical ensemble

Let us consider the nonrelativistic ideal gas of N identical particles governed by the classical Maxwell-Boltzmann statistics in the framework of the Tsallis and Boltzmann-Gibbs statistics in the microcanonical ensemble. For this special model, the statistical weight (111) can be written as (see [6] and reference therein)

$$W = \frac{(gV)^N}{N!}\left(\frac{m}{2\pi}\right)^{\frac{3}{2}N}\frac{E^{\frac{3}{2}N-1}}{\Gamma\left(\frac{3}{2}N\right)}, \tag{122}$$

http://dx.doi.org/10.5772/60997

where m is the particle mass. Then the entropies of the ideal gas for the Tsallis and Boltzmann-Gibbs statistics are calculated by Eqs. (112), (113), and (122).

The temperatures (Eqs. (114) and (115)) for the ideal gas for the Tsallis and Boltzmann-Gibbs statistics in the microcanonical ensemble correspond to [6]

$$T = \frac{EW^{1/z}}{3N/2-1} \qquad \text{for } |z| < \infty, \tag{123}$$

$$T = \frac{E}{3N/2-1} \qquad \text{for } |z| = \infty. \tag{124}$$

The pressures (Eqs. (116) and (117)) and the chemical potentials (Eqs. (118) and (119)) for the ideal gas for the Tsallis and Boltzmann-Gibbs statistics in the microcanonical ensemble can be written as [6]

$$p = \frac{N}{V}\frac{E}{3N/2-1} \qquad \text{for } |z| < \infty \text{ and } |z| = \infty, \tag{125}$$

$$\mu = -\frac{E}{3N/2-1}\left[\ln\left(gV\left(\frac{mE}{2\pi}\right)^{3/2}\right) - \psi(N+1) - \frac{3}{2}\psi\left(\frac{3}{2}N\right)\right] \qquad \text{for } |z| < \infty \text{ and } |z| = \infty. \tag{126}$$

The variable (Eq. (120)) for the ideal gas for the Tsallis statistics in the microcanonical ensemble is [6]

$$\Xi = -\frac{E}{3N/2-1}\left[1 - W^{1/z} + \ln W^{1/z}\right] \qquad \text{for } |z| < \infty. \tag{127}$$

However, the variable (Eq. (121)) for the Boltzmann-Gibbs statistics vanishes, $\Xi = 0$.

4.2.2. Nonrelativistic ideal gas in the thermodynamic limit: microcanonical ensemble

Let us rewrite the thermodynamic quantities of the nonrelativistic ideal gas in the microcanonical ensemble in the terms of the thermodynamic limit when the entropic parameter z is considered to be an extensive variable of state

$$\begin{aligned} &E \to \infty,\ V \to \infty,\ N \to \infty,\ |z| \to \infty, \\ &\varepsilon = \frac{E}{N} = const,\ v = \frac{V}{N} = const,\ \tilde{z} = \frac{z}{N} = const. \end{aligned} \tag{128}$$

Then in the thermodynamic limit (Eq. (128)), the statistical weight (Eq. (122)) for the nonrelativistic ideal gas can be rewritten as [6]

$$W = w^N, \qquad w \equiv gv\left(\frac{m\varepsilon e^{5/3}}{3\pi}\right)^{3/2}. \tag{129}$$

Substituting Eq. (129) into Eqs. (112) and (113) and using Eq. (128), we obtain the entropy as [6]

$$S = N\tilde{z}\left(1 - w^{-1/\tilde{z}}\right) \qquad \text{for } |\tilde{z}| < \infty, \tag{130}$$

$$S = N \ln w \qquad \text{for } |\tilde{z}| = \infty. \tag{131}$$

The temperatures (Eqs. (123) and (124)) for the nonrelativistic ideal gas in the thermodynamic limit (128) can be rewritten as [6]

$$T = \frac{2}{3}\varepsilon w^{1/\tilde{z}} \qquad \text{for } |\tilde{z}| < \infty, \tag{132}$$

$$T = \frac{2}{3}\varepsilon \qquad \text{for } |\tilde{z}| = \infty. \tag{133}$$

The pressure (125) and the chemical potential (126) for the nonrelativistic ideal gas in the thermodynamic limit (128) become [6]

$$p = \frac{2}{3}\frac{\varepsilon}{v} \qquad \text{for } |\tilde{z}| < \infty \text{ and } |\tilde{z}| = \infty, \tag{134}$$

$$\mu = \frac{2}{3}\varepsilon\left(\frac{5}{2} - \ln w\right) \qquad \text{for } |\tilde{z}| < \infty \text{ and } |\tilde{z}| = \infty. \tag{135}$$

The variable (Eq. (127)) for the Tsallis statistics in the thermodynamic limit (Eq. (128)) corresponds to [6]

$$\Xi = -\frac{2}{3}\varepsilon\left[1 - w^{1/\tilde{z}} + \ln w^{1/\tilde{z}}\right] \qquad \text{for } |\tilde{z}| < \infty. \tag{136}$$

http://dx.doi.org/10.5772/60997

For the Boltzmann-Gibbs statistics, we have $\Xi=0$. Using the results so far obtained for the Tsallis statistics given in Eqs. (130), (132), and (134)-(136), we can verify that the Euler theorem defined in Eqs. (22) and (98) is satisfied [6], i.e., $TS=E+pV-\mu N+\Xi z$.

Let us verify the principle of additivity for the nonrelativistic ideal gas in the microcanonical ensemble in the thermodynamic limit when the entropic parameter z is an extensive variable of state. Suppose that the system is divided into two subsystems (1 and 2). Then the extensive variables of state of the microcanonical ensemble are additive [6]

$$E^{1+2}=E^1+E^2,\quad V^{1+2}=V^1+V^2,\quad N^{1+2}=N^1+N^2,\quad z^{1+2}=z^1+z^2. \tag{137}$$

However, the specific variables of state (Eq. (128)) are the same in each subsystem (intensive)

$$\varepsilon^{1+2}=\varepsilon^1=\varepsilon^2,\quad v^{1+2}=v^1=v^2,\quad \tilde{z}^{1+2}=\tilde{z}^1=\tilde{z}^2. \tag{138}$$

Considering Eqs. (129), (137), and (138), we can verify that the Tsallis thermodynamic potential (Eq. (130)) of the microcanonical ensemble is a homogeneous function of the first order, i.e., $S(E,\,V,\,N,\,z)/N=S(\varepsilon,\,v,\,\tilde{z})$, and it is additive (extensive) [6]

$$S^{1+2}\left(E^{1+2},V^{1+2},N^{1+2},z^{1+2}\right)=S^1\left(E^1,V^1,N^1,z^1\right)+S^2\left(E^2,V^2,N^2,z^2\right). \tag{139}$$

Now, considering Eqs. (129), (137), and (138), we find that the Tsallis temperature (Eq. (132)), the pressure (Eq. (134)), the chemical potential (Eq. (135)), and the variable (Eq. (136)) are the homogeneous functions of the zero order, i.e., $T(E,\,V,\,N,\,z)=T(\varepsilon,\,v,\,\tilde{z})$, $p(E,\,V,\,N,\,z)=p(\varepsilon,\,v,\,\tilde{z})$, $\mu(E,\,V,\,N,\,z)=\mu(\varepsilon,\,v,\,\tilde{z})$, and $\Xi(E,\,V,\,N,\,z)=\Xi(\varepsilon,\,v,\,\tilde{z})$, respectively, and they are the same in each subsystem (intensive) [6]

$$T^{1+2}\left(E^{1+2},V^{1+2},N^{1+2},z^{1+2}\right)=T^1\left(E^1,V^1,N^1,z^1\right)=T^2\left(E^2,V^2,N^2,z^2\right), \tag{140}$$

$$p^{1+2}\left(E^{1+2},V^{1+2},N^{1+2},z^{1+2}\right)=p^1\left(E^1,V^1,N^1,z^1\right)=p^2\left(E^2,V^2,N^2,z^2\right), \tag{141}$$

$$\mu^{1+2}\left(E^{1+2},V^{1+2},N^{1+2},z^{1+2}\right)=\mu^1\left(E^1,V^1,N^1,z^1\right)=\mu^2\left(E^2,V^2,N^2,z^2\right), \tag{142}$$

$$\Xi^{1+2}\left(E^{1+2},V^{1+2},N^{1+2},z^{1+2}\right)=\Xi^1\left(E^1,V^1,N^1,z^1\right)=\Xi^2\left(E^2,V^2,N^2,z^2\right). \tag{143}$$

Thus, the principle of additivity (Eqs. (21), (24), and (25)) is totally satisfied by the Tsallis statistics in the microcanonical ensemble. Equation (140) proves the zero law of thermodynamics for the microcanonical ensemble [6].

4.3. Equivalence of canonical and microcanonical ensembles

We can now easily prove the equivalence of the canonical and microcanonical ensembles for the Tsallis statistics in the thermodynamic limits (Eqs. (82) and (128)). Using Eqs. (83) and (129), it is easy to verify that Eq. (132) for the temperature of the microcanonical ensemble and Eq. (86) for the energy of canonical ensemble are identical. Comparing Eqs. (83) and (129) and using Eq. (86), we have

$$w = \left(\tilde{Z}_G e^{3/2}\right)^{\frac{\tilde{z}}{\tilde{z}+\frac{3}{2}}}. \tag{144}$$

Substituting Eq. (144) into Eq. (130) for the entropy of the microcanonical ensemble, we obtain the entropy of the canonical ensemble (Eq. (90)). Equation (134) for the pressure of the microcanonical ensemble is identical to Eq. (92) for the pressure of the canonical ensemble. Substituting Eqs. (144) and (86) into Eq. (135) for the chemical potential of the microcanonical ensemble, we obtain Eq. (94) for the chemical potential of the canonical ensemble. Moreover, substituting Eqs. (144) and (86) into Eq. (136) for the variable Ξ of the microcanonical ensemble, we obtain Eq. (96) for the variable Ξ of the canonical ensemble. Thus, for the Tsallis statistics, the canonical and microcanonical ensembles are equivalent in the thermodynamic limit when the entropic parameter z is considered to be an extensive variable of state.

5. Conclusions

In conclusion, let us summarize the main principles of the equilibrium statistical mechanics based on the generalized statistical entropy. The basic idea is that in the thermodynamic equilibrium, there exists a universal function called thermodynamic potential that completely describes the properties and states of the thermodynamic system. The fundamental thermodynamic potential, its arguments (variables of state), and its first partial derivatives with respect to the variables of state determine the complete set of physical quantities characterizing the properties of the thermodynamic system. The physical system can be prepared in many ways given by the different sets of the variables of state and their appropriate thermodynamic potentials. The first thermodynamic potential is obtained from the fundamental thermodynamic potential by the Legendre transform. The second thermodynamic potential is obtained by the substitution of one variable of state with the fundamental thermodynamic potential. Then the complete set of physical quantities and the appropriate thermodynamic potential determine the physical properties of the given system and their dependences. In the equilibrium thermodynamics, the thermodynamic potential of the physical system is given a priori, and it is a multivariate function of several variables of state. However, in the equilibrium

statistical mechanics, the thermodynamic potential is a composed function that can depend on the set of independent variables of state explicitly and implicitly through the probabilities of microstates. The probabilities of microstates are determined from the second part of the second law of thermodynamics, i.e., the maximum entropy principle. The equilibrium probability distributions are found from the constrained extremum of the thermodynamic potential as a function of a multidimensional set of probabilities considering that the statistical entropy is defined. The equilibrium thermodynamics and statistical mechanics are defined only on the class of homogeneous functions, i.e., all thermodynamic quantities describing the thermodynamic system should belong to the class of homogeneous functions of the first or zero orders.

In the present work, the general mathematical scheme of construction of the equilibrium statistical mechanics on the basis of an arbitrary definition of statistical entropy for two types of thermodynamic potential, the first and the second thermodynamic potentials, was proposed. As an example, we investigated the Tsallis and Boltzmann-Gibbs statistical entropies in the canonical and microcanonical ensembles. On the example of a nonrelativistic ideal gas, it was proven that the statistical mechanics based on the Tsallis entropy satisfies the requirements of the equilibrium thermodynamics only in the thermodynamic limit when the entropic index z is an extensive variable of state of the system. In this case the thermodynamic quantities of the Tsallis statistics belong to one of the classes of homogeneous functions of the first or zero orders.

Acknowledgements

This work was supported in part by the joint research project of JINR and IFIN-HH, protocol N 4342.

Author details

A.S. Parvan[1,2,3]

Address all correspondence to: parvan@theor.jinr.ru

1 Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna, Russian Federation

2 Department of Theoretical Physics, Horia Hulubei National Institute of Physics and Nuclear Engineering, Bucharest-Magurele, Romania

3 Institute of Applied Physics, Moldova Academy of Sciences, Chisinau, Republic of Moldova

References

[1] Gibbs J W. Elementary Principles in Statistical Mechanics, Developed with Especial Reference to the Rational Foundation of Thermodynamics. New Haven: Yale University Press; 1902

[2] Balescu R. Equilibrium and Nonequilibrium Statistical Mechanics. New York: Wiley; 1975.

[3] Tsallis C. Possible generalization of Boltzmann-Gibbs statistics. J. Stat. Phys. 1988;52(1-2):479-487.

[4] Tsallis C, Mendes R S, Plastino A R. The role of constraints within generalized nonextensive statistics. Physica A. 1998;261(3-4):534-554.

[5] Abe S, Martinez S, Pennini F, Plastino A. Classical gas in nonextensive optimal Lagrange multipliers formalism. Phys. Lett. A. 2001;278(5):249-254.

[6] Parvan A S. Microcanonical ensemble extensive thermodynamics of Tsallis statistics. Phys. Lett. A. 2006;350(5-6):331-338.

[7] Parvan A S. Extensive statistical mechanics based on nonadditive entropy: Canonical ensemble. Phys. Lett. A. 2006;360(1):26-34.

[8] Lenzi E K, Mendes R S, da Silva L R. Statistical mechanics based on Renyi entropy. Physica A. 2000;280(3-4):337-345.

[9] Parvan A S, Biro T S. Extensive Rényi statistics from non-extensive entropy. Phys. Lett. A. 2005;340(5-6):375-387.

[10] Parvan A S, Biro T S. Rényi statistics in equilibrium statistical mechanics. Phys. Lett. A. 2010;374(19-20):1951-1957.

[11] Wang Q A. Incomplete statistics: nonextensive generalizations of statistical mechanics. Chaos, Solitons and Fractals. 2001;12(8):1431-1437.

[12] Parvan A S, Biro T S. Equilibrium statistical mechanics for incomplete nonextensive statistics. Phys. Lett. A. 2011;375(3):372-378.

[13] Jaynes E T. Information Theory and Statistical Mechanics. II. Phys. Rev. 1957;108(2): 171.

[14] Prigogine I, Kondepudi D. Modern Thermodynamics: From Heat Engines to Dissipative Structures. Chichester: John Wiley & Sons; 1998.

[15] Kvasnikov I A. Thermodynamics and Statistical Mechanics: The Equilibrium Theory. Moscow: Moscow State Univ. Publ.; 1991.

[16] Botet R, Ploszajczak M, Gonzalez J A. Phase transitions in nonextensive spin systems. Phys. Rev. E. 2001;65(1):015103(R).

[17] Botet R, Ploszajczak M, Gudima K K, Parvan A S, Toneev V D. The thermodynamic limit in the non-extensive thermostatistics. Physica A. 2004;344(3-4):403-408.

[18] Krasnov M L, Makarenko G I, Kiseliov A I. Calculus of Variations: Problems and Exercises with detailed solutions. 2nd ed. Moscow: URSS Publisher; 2002.

[19] Arnold V I. Mathematical methods of classical mechanics. 2nd ed. New York : Springer-Verlag; 1989.

[20] Prigogine I, Defay R. Chemical Thermodynamics. London: Longmans, Green & Co Ltd; 1954.

IntechOpen

IntechOpen

IntechOpen