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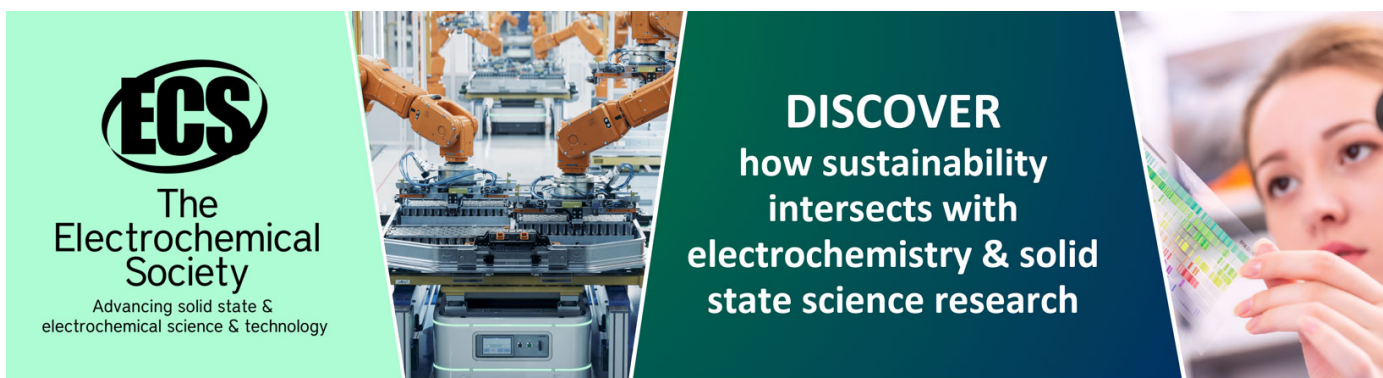
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To cite this article: J J Peña *et al* 2016 *J. Phys.: Conf. Ser.* **738** 012095

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On the generalization of statistical thermodynamic functions by a Riccati differential equation.

J J Peña, A Rubio-Ponce and J Morales

Universidad Autónoma Metropolitana - Azcapotzalco,
CBI - Area de Física Atómica Molecular Aplicada,
Av. San Pablo 180, 02200 México, D.F., MEXICO.

Corresponding author: jjpg@correo.azc.uam.mx

Abstract. In this work, we propose a non-linear differential equation of Riccati-type, where the standard partition function $Z(T)$ is taken as its particular solution leading to their generalization $Z_g(T)$; from there, other related statistical thermodynamic functions are generalized. As an useful application of our proposal, other thermodynamic functions, namely, the internal energy, heat capacity, Helmholtz free energy and entropy, associated to the model of the ideal monatomic gas in D -dimensions are generalized. According to our results, thermodynamic properties derived from the standard partition functions by means of ordinary statistical mechanics are incomplete. In fact, although asymptotically with the increasing of temperature the generalized statistical thermodynamic functions reduce to the standard ones, these contain an extra term which is dominant at very low temperature indicating that standard findings should be corrected.

PACS: 05.30.-d, 03.65.Fd, 51.30.+i.

Keywords: Thermodynamic functions, Riccati equation.

1. Introduction

In statistical mechanics, almost all thermodynamic properties of a system can be obtained from the standard partition function $Z(T)$ which is related with the standard internal energy of the system $U(T)$ through the derivative of $\ln Z(T)$ [1]. This means that the existence of a partition function guarantees the knowledge of the thermodynamic properties of system [2]. This statement seems to be equivalent to that of quantum mechanics about solvable potentials, which establish that a potential is exactly solvable on condition of having an associated Witten superpotential [3,4]. In that case, the choice of the Witten superpotential as a particular solution of the involved Riccati equation leads us to identify the potential under study [5], to generalize the former potential as well as to find their isospectral partners [6]. Thus, because we are interested on the generalization of thermodynamic partition functions, we propose to follow a similar treatment to the one outlined above [7]. That is, the aim of this work is to propose a nonlinear differential equation of Riccati type where the thermodynamic variables $U(T)$ and $Z(T)$ are involved in such a way that all other thermodynamic properties of a system, that come from $Z(T)$ or $U(T)$, can be generalized. In next section, the equations that generalize the partition function and the internal energy are presented along with the generalized equations that correspond to the entropy, specific heat and Helmholtz free energy. As an useful application of the proposed Riccati-type equation for statistical thermodynamics, in section III we consider the



generalized statistical thermodynamic properties of the ideal monatomic gas in one, two and three dimensions. Although this statistical model is always considered in every modern textbook on statistical mechanics, the theory of ideal quantum gases is far from being a closed field for research [8,9]. Moreover, the proposed equations can be directly used to generalize other statistical models as well as to find new partition functions that could be useful in the treatment of some relevant thermodynamic applications.

2. Partition function

In a thermodynamic system at equilibrium, the canonical partition function $Z(T)$, which is given in terms of thermodynamic state variables, plays an important role in statistical physics due that all the thermodynamic functions associated to a statistical system, such as entropy, internal energy, free energy, heat capacity and others are obtained in terms of $Z(T)$ and its derivatives [10]. Consequently, the $Z(T)$ along with the particular properties of each system leads to the so-called equation of state that completely characterizes the system under study. The partition function for a classical discrete system is given by the equation

$$Z(T) = \sum_i e^{-\frac{E_i}{kT}} \quad (1)$$

where E_i is the energy of the system in a state i and k is the Boltzman constant. Thus defined, the partition function has a probabilistic sense because the factor $e^{-\frac{E_i}{kT}}$ is interpreted as the probability that the system is in a state i with energy E_i , i.e.

$$P_i = C e^{-\frac{E_i}{kT}}, \quad (2)$$

where C is a constant of proportionality. In the case we are studying, the partition function $Z(T)$ plays the role of the normalization constant for the probability distribution in question Eq. (2). Indeed, if we apply the fact that the sum of all probabilities is the unity,

$$\sum_i P_i = 1, \quad (3)$$

then

$$\sum_i P_i = \sum_i C e^{-\frac{E_i}{kT}} = C \sum_i e^{-\frac{E_i}{kT}} = 1 \Rightarrow C = \frac{1}{\sum_i e^{-\frac{E_i}{kT}}} = \frac{1}{Z(T)} \quad (4)$$

such that the normalized probability distribution is

$$P_i = \frac{e^{-\frac{E_i}{kT}}}{\sum_i e^{-\frac{E_i}{kT}}} = \frac{1}{Z(T)} e^{-\frac{E_i}{kT}} \quad (5)$$

With this probability distribution, it is possible to calculate average values of various amounts of interest, such of the ones that we are going to show next and which will be useful for the purpose of this paper.

2.1. Calculations of average values for the energy.

As mentioned earlier, starting from the partition function and its derivatives, it is possible to deduce the thermodynamic functions of statistical mechanics. Indeed, based on the probability distribution of Eq. (5), the average value of energy $\langle E \rangle = \bar{E} = U$ is given by

$$U = \sum_i P_i E_i = \sum_i \frac{E_i e^{-\frac{E_i}{kT}}}{Z(T)} = \frac{1}{Z} \sum_i kT^2 \frac{\partial e^{-\frac{E_i}{kT}}}{\partial T} = \frac{kT^2}{Z(T)} \frac{\partial Z(T)}{\partial T} = kT^2 \frac{\partial \ln Z(T)}{\partial T}. \quad (6)$$

Similarly to the above equation, $\langle E^2 \rangle = \overline{E^2}$, which is different of $\langle E \rangle^2 = (\bar{E})^2 = U^2$, becomes as

$$\langle E^2 \rangle = \sum_i P_i E_i^2 = \frac{1}{Z} \sum_i E_i^2 e^{-\frac{E_i}{kT}}. \quad (7)$$

However, by noticing that

$$\frac{\partial^2 Z(T)}{\partial T^2} = \left(\frac{1}{kT^2} \right)^2 \sum_i E_i^2 e^{-\frac{E_i}{kT}} - \frac{2}{kT^3} \sum_i E_i e^{-\frac{E_i}{kT}}, \quad (8)$$

it can be rewritten as

$$\frac{\partial^2 Z(T)}{\partial T^2} = \left(\frac{1}{kT^2} \right)^2 Z(T) \left(\frac{\sum_i E_i^2 e^{-\frac{E_i}{kT}}}{Z(T)} \right) - \frac{2 Z(T)}{kT^3} \left(\frac{\sum_i E_i e^{-\frac{E_i}{kT}}}{Z(T)} \right), \quad (9)$$

the expectation value of the square energy given in Eq.(7) will be

$$\langle E^2 \rangle = (kT^2)^2 \left(\frac{\frac{\partial^2 Z(T)}{\partial T^2}}{Z(T)} \right) + 2kT \langle E \rangle. \quad (10)$$

Also,

$$\frac{\frac{\partial^2 Z}{\partial T^2}}{Z} = \frac{1}{Z} \frac{\partial}{\partial T} \left(\frac{Z}{kT^2} kT^2 \left(\frac{\partial Z}{\partial T} \right) \right) = \frac{1}{Z} \frac{\partial}{\partial T} \left(\frac{Z}{kT^2} \langle E \rangle \right), \quad (11)$$

leads to

$$(kT^2)^2 \left(\frac{\frac{\partial^2 Z(T)}{\partial T^2}}{Z(T)} \right) = kT^2 \frac{\partial \langle E \rangle}{\partial T} + \langle E \rangle^2 - 2kT \langle E \rangle. \quad (12)$$

Finally, we want to point out that the combination of Eqs. (10) and (12) allow us the calculation of fluctuations or dispersion of the energy $\overline{(\Delta E)^2}$, i.e.

$$\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \overline{E^2 - 2E\bar{E} + \bar{E}^2} = \langle E^2 \rangle - \langle E \rangle^2 \quad (13)$$

from where

$$\overline{(\Delta E)^2} = kT^2 \frac{\partial \langle E \rangle}{\partial T} = kT^2 \frac{\partial U}{\partial T}. \quad (14)$$

2.2. The canonical partition function and the Riccati equation.

As can be seen, Eq.(12) can be written as

$$\frac{1}{kT^2} \frac{\partial U}{\partial T} - \frac{2}{kT^3} U + \left(\frac{U}{kT^2} \right)^2 = \frac{Z(T)''}{Z(T)}, \text{ with } Z(T)'' = \frac{\partial^2 Z(T)}{\partial T^2} \quad (15)$$

which means

$$\frac{\partial}{\partial T} \left(\frac{U}{kT^2} \right) + \left(\frac{U}{kT^2} \right)^2 = \frac{Z''}{Z}. \quad (16)$$

At this point, it is interesting to notice that the definition of a new thermodynamic function

$$R(T) = \frac{U(T)}{kT^2} \quad (17)$$

indicates that Eq. (16) becomes a Riccati equation

$$R'(T) + R^2(T) = \frac{Z''(T)}{Z(T)} \quad (18)$$

from where it is possible to generalize different statistical thermodynamic functions as will see next.

3. On the generalization of statistical thermodynamic functions

Let us consider the Riccati relationship

$$y'(x) + y^2(x) = f(x), \quad (19)$$

if a particular solution $y_p(x)$ is known, then the general solution is given by [11]

$$y_g(x) = y_p(x) + \frac{b}{e^{2 \int y_p dx} \left(1 + b \int \frac{dx}{e^{2 \int y_p dx}} \right)} = y_p(x) + \frac{d}{dx} \ln \left(1 + b \int \frac{dx}{e^{2 \int y_p dx}} \right). \quad (20)$$

where the index g indicates general or generalized.

So, regarding with Eq.(18), by assuming $y_p(x) = R(T)$ this means that

$$R_g(T) = R(T) + \frac{b}{e^{2 \int R(T) dT} \left(1 + b \int \frac{dT}{e^{2 \int R(T) dT}} \right)}. \quad (21)$$

Moreover, due that according to Eq.(6) $U = kT^2 \frac{\partial \ln Z(T)}{\partial T}$, or the equivalent $R(T) = \frac{Z'(T)}{Z(T)}$, there exist also $Z_g(T)$ such that

$$Z_g(T) = Z(T) \left(1 + b \int \frac{dT}{Z^2(T)} \right). \quad (22)$$

In fact Eq.(21) can be written as

$$\begin{aligned} R_g(T) &= \frac{Z'(T)}{Z(T)} + \frac{b}{e^{2 \int R(T) dT} \left(1 + b \int \frac{dT}{e^{2 \int R(T) dT}} \right)} = \frac{d}{dT} \ln Z(T) + \frac{d}{dT} \ln \left(1 + b \int \frac{dT}{Z^2(T)} \right) \\ &= \frac{d}{dT} \ln \left(Z(T) \left(1 + b \int \frac{dT}{Z^2(T)} \right) \right) = \frac{d}{dT} \ln(Z_g(T)), \end{aligned} \quad (23)$$

that is to say

$$R_g(T) = \frac{Z'_g(T)}{Z_g(T)}, \quad (24)$$

leading to the generalization of Eq.(18)

$$R'_g(T) + R_g^2(T) = \frac{Z''_g(T)}{Z_g(T)}. \quad (25)$$

Consequently, this means that all the statistical thermodynamic functions associated with $R_g(T)$ can be straightforward generalized such as happen from Eq.(17)

$$U_g(T) = kT^2 R_g(T) = kT^2 \frac{d}{dT} \ln Z_g(T) \quad (26)$$

that corresponds to the generalization of the internal energy of the system. In a similar way, other important statistical thermodynamic properties, related with the partition function, the internal energy

and their derivatives, can be generalized. For example, the entropy $S(T)$, the Helmholtz free energy $F(T)$ and the heat capacity $C(T)$ are related with $Z(T)$ and $Z_g(T)$ as follow

$$S(T) = -\frac{d}{dT} Z(T) \rightarrow S_g(T) = k \ln Z_g(T) + \frac{U_g(T)}{T}, \quad (27)$$

$$F(T) = -kT \ln Z(T) \rightarrow F_g(T) = -kT \ln Z_g(T) \quad (28)$$

and

$$C(T) = \frac{d}{dT} U(T) = T \frac{d}{dT} S(T) = -T \frac{d^2}{dT^2} F(T) \rightarrow C_g(T) = \frac{d}{dT} U_g(T). \quad (29)$$

In short, by using Eq.(22) the above generalized statistical thermodynamic functions are written as

$$Z_g(T) = Z(T) + bZ(T) \int \frac{dT}{Z^2(T)}, \quad (30)$$

$$U_g(T) = U(T) + kT^2 \frac{d}{dT} \ln \left(1 + b \int \frac{dT}{Z^2(T)} \right), \quad (31)$$

$$S_g(T) = S(T) + \frac{d}{dT} \left(kT \ln \left(1 + b \int \frac{dT}{Z^2(T)} \right) \right), \quad (32)$$

$$F_g(T) = F(T) - kT \ln \left(1 + b \int \frac{dT}{Z^2(T)} \right) \quad (33)$$

and

$$C_g(T) = C(T) + T \frac{d^2}{dT^2} \left(kT \ln \left(1 + b \int \frac{dT}{Z^2(T)} \right) \right). \quad (34)$$

As can be appreciated, the generalized statistical thermodynamic functions contain, algebraically, the corresponding standard functions plus an additional term which depends on temperature.

4. Applications

In this section, we will apply the above results to the system of an ideal gas with N particles confined in a container. In this case, the internal energy is given by

$$U(T) = \frac{DN}{2} kT \quad (35)$$

where D indicates the degrees of freedom of particles such that $D = 1, 2, 3$ corresponds to 1, 2 and 3 dimensions respectively. Thus, using Eqs.(6) and (17), the standard partition function becomes

$$Z(T) = e^{\int R(T) dT} = (AT)^{\frac{DN}{2}} \quad (36)$$

where A is a proper constant that leaves $Z(T)$ dimensionless. Accordingly to Eq.(22), the generalized partition function is given by

$$Z_g(T) = Z(T) + \frac{(Z(T))^{\frac{2}{DN}-1}}{DN-1}. \quad (37)$$

In consequence, the generalized statistical thermodynamic functions for the model of ideal gas in D dimensions are

$$Z_g(T) = (AT)^{\frac{DN}{2}} + \frac{(AT)^{1-\frac{DN}{2}}}{DN-1} \quad (38)$$

$$U_g(T) = \frac{DN}{2} kT - \frac{(DN-1)kT}{(DN-1)(AT)^{DN-1+1}} \quad (39)$$

$$S_g(T) = \frac{DN}{2} k + k \ln[(AT)^{\frac{DN}{2}}] + k \ln[1 + \frac{(AT)^{-(DN-1)}}{(DN-1)}] - \frac{(DN-1)k}{(DN-1)(AT)^{DN-1+1}} \quad (40)$$

$$F_g(T) = -kT \ln[(AT)^{\frac{DN}{2}}] - kT \ln[1 + \frac{(AT)^{-(DN-1)}}{(DN-1)}] \quad (41)$$

and

$$C_g(T) = \frac{DN}{2} k + k \frac{(DN-1)^2(DN-2)(AT)^{DN-1-(DN-1)}}{((DN-1)(AT)^{DN-1+1})^2}. \quad (42)$$

From these results, it becomes evident that all the above generalized statistical thermodynamic functions tend asymptotically to the corresponding standard ones for a temperature beyond of which the generalized partition function reach its minimum. Namely, from Eq. (38) the minimum value of $Z_g(T)$ is obtained by solving the equation $Z'_g(T) = 0$ such that

$$Z_{gMin} = Z_g(T_{MinZg}) = \left(\frac{DN-2}{DN(DN-1)} \right)^{\frac{DN}{2(DN-1)}} + \frac{\left(\frac{DN-2}{DN(DN-1)} \right)^{\frac{2-DN}{2(DN-1)}}}{DN-1}, \quad (43)$$

where T_{MinZg} is the temperature at which $Z_g(T)$ reach its minimum given by

$$T_{MinZg} = \frac{1}{A} \left(\frac{DN-2}{DN(DN-1)} \right)^{\frac{1}{3N-1}}. \quad (44)$$

Likewise, due that $U_g = kT^2 Z'_g / Z_g$ such that $U_g(T_{RootUg}) = 0$, it leads to $T_{RootUg} = T_{MinZg}$ where T_{RootUg} is the temperature at which U_g has a root, i.e. where U_g is null. Also, in the interval $(0, T_{RootUg})$ $U_g < 0$, reaching in this range a minimum value

$$U_{gMin} = \frac{k}{A} \left(\sqrt{\frac{DN(DN-2)+((DN-1)^2+1)^2}{(DN(DN-1))^2}} - \frac{(DN-1)^2+1}{DN(DN-1)} \right)^{\frac{1}{DN-1}} \left(\frac{DN}{2} - \frac{DN(DN-1)}{\sqrt{DN(DN-2)+((DN-1)^2+1)^2} - (DN-1)(DN-2)} \right) \quad (45)$$

at T_{MinUg} which is the temperature where $U_g(T)$ is minimal. That is $U'_g(T_{MinUg}) = 0$ leading to

$$T_{MinUg} = A^{-1} \left(\sqrt{\frac{DN(DN-2)+((DN-1)^2+1)^2}{(DN(DN-1))^2}} - \frac{(DN-1)^2+1}{DN(DN-1)} \right)^{\frac{1}{DN-1}}. \quad (46)$$

Besides, due that according to Eq. (29) $C_g(T) = U'_g(T)$, then $C_g(T_{MinUg}) = U'_g(T_{MinUg}) = 0$ this implies that $T_{MinUg} = T_{RootCg}$ which is the temperature at where C_g is null.

At this point, it is worth mentioning that by combining Eqs. (26) and (29) one has

$$C_g(T) = \frac{d}{dT} U_g(T) = \frac{d}{dT} \left(kT^2 \frac{d}{dT} \ln Z_g(T) \right), \quad (47)$$

that permits to select the interval of validity of our equations. Finally, the heat capacity has a maximal value given by

$$C_{gMax} = C_g(T_{MaxCg}) = \frac{DN}{2} k + \left(\frac{DN}{2} - 1 \right)^2 k \quad (48)$$

where T_{MaxCg} can be obtained from Eq. (42) after solving $C'_g(T) = 0$ as

$$T_{MaxCg} = A^{-1} \left(\frac{DN}{(DN-1)(DN-2)} \right)^{\frac{1}{DN-1}}. \quad (49)$$

In short, we want to notice that a similar study can be done directly from the proposed generalized partition or internal energy functions to other statistical thermodynamic properties different to those considered in this work as well as to other model systems [12].

5. Concluding remarks

Starting from the basic definitions of statistical mechanics, in this paper we propose a non-linear differential equation of Riccati-type involving the statistical thermodynamic functions of internal energy and partition function. To achieve this, it is used an $R(T)$ function linking both the internal energy as the partition function through the logarithmic derivative $R(T) = Z' / Z$. This same function is taken as a particular solution in order to find a general solution of the Riccati-type equation. So, this general solution leads to the generalization of the partition function $Z_g(T)$ and the internal energy $U_g(T)$. From there, the thermodynamic properties associated with these functions are directly generalized; specifically we consider the generalization of entropy, Helmholtz free energy and heat capacity in the case of the ideal monatomic gas in D-dimensions. According to our results, the statistical thermodynamic properties derived from the standard partition functions by means of ordinary statistical mechanics are incomplete, therefore should be corrected with the generalized equations that contain an extra term which is dominant at very low temperature. Besides, our proposal is general and can be directly applied to other thermodynamic models.

Acknowledgment

This work was partially supported by the projects UAM-A-CBI-2232004 and 009. We are grateful with SNI-Conacyt-México for the stipend received.

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