

# Entropic Formulation of Statistical Mechanics.

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## Abstract

We present an alternative formulation of equilibrium statistical mechanics which may have some pedagogical advantages. It follows the method based on the maximum statistical entropy principle in Information Theory combined with the use of Massieu-Planck functions. The different statistical ensembles are obtained by a suitable restriction of the whole set of available microstates. The main advantage is that all the equations relating the average values with derivatives of the partition function are formally identical in the different ensembles. Two examples are solved within the proposed framework.

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## I. INTRODUCTION

The central equation in Equilibrium Statistical Mechanics identifies the thermodynamic entropy  $S$  with the maximum value  $\mathcal{S}$  of the statistical entropy functional  $\hat{\mathcal{S}}(\{p_i\})$  through the Boltzmann constant  $k$  [1]:

$$\frac{S}{k} = \mathcal{S}. \quad (1)$$

The thermodynamic entropy  $S$  is a quantity defined for equilibrium (macro)states of a system. On the other hand, the statistical entropy functional  $\hat{\mathcal{S}}(\{p_i\})$  characterizes the uncertainty associated with any probability distribution  $\{p_i\}$  defined on the set of available microstates  $\Omega = \{i\}$ . It takes the general form:

$$\hat{\mathcal{S}}(\{p_i\}) = - \sum_{i \in \Omega} p_i \ln p_i \quad (2)$$

where  $p_i$  satisfy the normalization condition  $\sum_{i \in \Omega} p_i = 1$ .

This formulation of Equilibrium Statistical Mechanics corresponds, within the context of Information Theory, to the so called Maximum Statistical Entropy Principle [2]. Actually, Eq. (2) is a definition that naturally arises within this framework by requiring the following conditions: (i)  $\hat{\mathcal{S}}$  must be positive and takes the value zero only in the case of absolute certainty ( $p_i = 0$  for all the states, except for a given state  $j$  for which  $p_j = 1$ ); (ii)  $\hat{\mathcal{S}}$  must increase monotonically with increasing uncertainty; and (iii) it must be additive for independent sources of uncertainty (extensivity).

It should be pointed out that the equality (1) only holds for extensive macroscopic (thermodynamic limit) systems. Nevertheless, an extension of this formulation to the case of non-extensive thermodynamics can be done by alternative definitions of the statistical entropy functional [3].

In the particular case of an isolated hydrostatic pure substance, the available microstates ( $\Omega_{E,V,N}$ ) are those with a fixed energy  $E$ , volume  $V$  and number of particles  $N$ . It is easy to show that the maximum entropy  $\mathcal{S}$  is obtained when all the microstates have equal

probability  $p_i = \frac{1}{\mathcal{W}}$ , where  $\mathcal{W}$  is the number of microstates in  $\Omega_{E,V,N}$ . Therefore, in this case, equation (1) reduces to the well-known equation already proposed by Boltzmann in 1877 [4]:

$$S(E, V, N) = k \ln \mathcal{W} \quad (3)$$

This is the basic equation of the so-called Microcanonical Ensemble. Other statistical ensembles are introduced by relaxing constraints regarding the interaction of the system with the surroundings, which increases the set of compatible microstates. For instance, in the Canonical Ensemble the system is permitted to exchange energy with a reservoir, provided that its mean energy  $U = \sum_{i \in \Omega_{V,N}} p_i E_i$  is fixed ( $E_i$  are the eigenvalues of the system Hamiltonian). The available microstates are those with fixed  $V$  and  $N$ , thus  $\Omega_{V,N} \supset \Omega_{E,V,N}$  [5]. In the derivation of the corresponding basic equation, the temperature  $T$  appears naturally as a parameter controlling the mean energy. The resulting equation relates the Helmholtz free energy  $F = U - TS$  with the logarithm of the partition function  $Q_C$  [6,7]:

$$F(T, V, N) = -kT \ln Q_C \quad (4)$$

with:

$$Q_C = \sum_{i \in \Omega_{V,N}} e^{-\frac{E_i}{kT}}. \quad (5)$$

In a similar way one can derive the Grand Canonical Ensemble by allowing the exchange of energy and particles, by fixing the mean energy  $U$  and mean number of particles  $N$ . In such ensembles the thermodynamic variables determining the macrostate of the system are usually taken as natural variables of an energetic potential. This is in contrast with the Microcanonical Ensemble where entropy is taken as the relevant potential. Consequently the corresponding basic equations of such ensembles are formally different, as can be seen by comparing equations (3) and (4). Therefore, all the equations derived for the average values and fluctuations of different microscopic quantities are also formally different.

The goal of the present paper is to show that if the different statistical ensembles are constructed choosing appropriate variables, the thermodynamic-statistical connection can

be established using an entropic potential through a basic equation formally identical to equation (3) for all the different ensembles. As will be shown, the relevant thermodynamic potentials in this case are Massieu-Planck functions [8] obtained by means of Legendre transformations of the entropy. Actually, the interest in Massieu-Planck functions in Statistical Mechanics was already mentioned in Callen's book [9]. However, standard textbooks [2,6,7,10–12] do not make use of them at all. An exception is Münster's book [13], where the formal treatment of Generalized Ensembles is based on Massieu-Planck functions, with a viewpoint that shares a number of similarities with the formulation presented here. The proposed systematics turn out to be especially adequate for calculations in ensembles such as the Grand Canonical or the Isobaric-Isothermal Ensembles, since the identification of proper pairs of entropic conjugate variables considerably simplifies the expressions determining average values and fluctuations.

Although there is nothing essential in the proposed development, its interest lies in rationalizing the formulation of Ensemble Theory by providing compact expressions for the different thermodynamic quantities which take exactly the same form in all statistical ensembles. The paper is organized as follows. In section II Massieu-Planck functions are introduced and in the next section the ensemble theory is formulated by making use of the previously introduced natural thermodynamic variables for Massieu-Planck functions. Finally, in section V two examples are discussed: the ideal gas in the Grand Canonical ensemble and the magnetic solid.

## II. ENTROPIC VARIABLES AND MASSIEU-PLANCK FUNCTIONS

We consider a simple pure substance under hydrostatic conditions described by the following fundamental equation:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN, \quad (6)$$

where the extensive variables  $U$ ,  $V$  and  $N$  are the internal energy, the volume, and the number of particles respectively, and the intensive variables  $T$ ,  $p$  and  $\mu$  are the temperature,

the pressure and the chemical potential respectively.

Equation (6) corresponds to the choice of the variables  $U$ ,  $V$  and  $N$  as independent variables of the entropy  $S(U, V, N)$ . These variables are precisely those which are fixed and determine the macrostate of the members of the Microcanonical Ensemble and consequently  $S$  is the relevant potential in this statistical ensemble.

It is useful to define the following quantities:  $\beta \equiv 1/kT$ ,  $\pi \equiv p/kT$  and  $\nu \equiv -\mu/kT$  so that Eq. (6) can then be written in the dimensionless form:

$$d\mathcal{S} = \beta dU + \pi dV + \nu dN. \quad (7)$$

In general, for other thermodynamic systems with  $\mathcal{N}$  degrees of freedom, one will have:

$$d\mathcal{S} = \sum_{k=1}^{\mathcal{N}} y_k dX_k, \quad (8)$$

where  $X_k$  are extensive variables, and  $y_k$  the corresponding entropic conjugate variables. Massieu-Planck functions [8] are entropic thermodynamic potentials defined as Legendre transformations of the entropy. In the case of a pure substance, the following (dimensionless) potentials can be formally defined:

$$\Phi(\beta, V, N) \equiv \mathcal{S} - \beta U, \quad (9)$$

$$\Lambda(U, \pi, N) \equiv \mathcal{S} - \pi V, \quad (10)$$

$$\Gamma(U, V, \nu) \equiv \mathcal{S} - \nu N, \quad (11)$$

$$\Xi(\beta, \pi, N) \equiv \mathcal{S} - \beta U - \pi V, \quad (12)$$

$$\Upsilon(U, \pi, \nu) \equiv \mathcal{S} - \pi V - \nu N, \quad (13)$$

$$\Psi(\beta, V, \nu) \equiv \mathcal{S} - \beta U - \nu N, \quad (14)$$

$$\Pi(\beta, \pi, \nu) \equiv \mathcal{S} - \beta U - \pi V - \nu N. \quad (15)$$

The function  $\Phi$  was first introduced by Massieu [14], and it is called Massieu's potential. The function  $\Xi$  was introduced by Planck [15] and is called Planck's. potential. Given the extensivity of  $\mathcal{S}$ , and using Euler's theorem for homogeneous functions, it is easy to see that  $\Pi = 0$ . Therefore the Legendre transformation of all variables redefines the entropy,

$$\mathcal{S} = \beta U + \pi V + \nu N. \quad (16)$$

Substituting Eq. (7) into the differentials of the potentials defined above one gets:

$$d\Phi = -Ud\beta + \pi dV + \nu dN \quad (17)$$

$$d\Lambda = \beta dU - Vd\pi + \nu dN \quad (18)$$

$$d\Gamma = \beta dU + \pi dV - Nd\nu \quad (19)$$

$$d\Xi = -Ud\beta - Vd\pi + \nu dN \quad (20)$$

$$d\Upsilon = \beta dU - Vd\pi - Nd\nu \quad (21)$$

$$d\Psi = -Ud\beta + \pi dV - Nd\nu, \quad (22)$$

From Eq. (16) one obtains:

$$Ud\beta + Vd\pi + Nd\nu = 0 \quad (23)$$

The above equations allow a re-derivation of all the standard thermodynamic equations in terms of  $\beta$ ,  $\pi$  and  $\nu$ . For instance, Maxwell relations can be deduced, by imposing that the equations (17)-(22) are exact differentials (equality of crossed derivatives). Moreover, Eq. (23) is the Gibbs-Duhem equation which states that the complete set of intensive variables of the system are not all independent. On the other hand, the extremal condition of  $\mathcal{S}$  leads us to deduce that  $\beta$ ,  $\pi$  and  $\nu$  are homogeneous at equilibrium [16].

### III. STATISTICAL MECHANICS

In contrast to most textbooks the statistical ensembles will be introduced by starting with the most generalized one (completely open system) and later imposing the constraints that lead to the standard statistical ensembles. Thus, we begin by studying the Generalized Ensemble in which the system can exchange energy, volume and particles with the surroundings but keeps the corresponding average values  $U$ ,  $V$  and  $N$  constant:

$$U \equiv \langle E \rangle = \sum_{i \in \Omega} p_i E_i, \quad (24)$$

$$\langle V \rangle = \sum_{i \in \Omega} p_i V_i, \quad (25)$$

$$\langle N \rangle = \sum_{i \in \Omega} p_i N_i. \quad (26)$$

Using the method of Lagrange multipliers we maximize the statistical entropy functional subject to the constraints (24),(25), (26) and the normalization condition of the probabilities  $p_i$ . This gives:

$$\frac{\partial \mathcal{L}}{\partial p_i} = 0, \quad (27)$$

where:

$$\mathcal{L}(\{p_i\}) = - \sum_{i \in \Omega} p_i \ln p_i - \lambda_0 \sum_{i \in \Omega} p_i - \lambda_1 \sum_{i \in \Omega} E_i p_i - \lambda_2 \sum_{i \in \Omega} V_i p_i - \lambda_3 \sum_{i \in \Omega} N_i p_i. \quad (28)$$

Note that, in this ensemble,  $\Omega$  corresponds to the set of microstates with any value for energy  $E_i$ , volume  $V_i$  and number of particles  $N_i$ . The following is obtained:

$$p_i = \frac{e^{-(\lambda_1 E_i + \lambda_2 V_i + \lambda_3 N_i)}}{\sum_{i \in \Omega} e^{-(\lambda_1 E_i + \lambda_2 V_i + \lambda_3 N_i)}}. \quad (29)$$

The value of the entropy at the maximum is:

$$\mathcal{S} = \left( \ln \sum_{i \in \Omega} e^{-(\lambda_1 E_i + \lambda_2 V_i + \lambda_3 N_i)} \right) + \lambda_1 U + \lambda_2 \langle V \rangle + \lambda_3 \langle N \rangle. \quad (30)$$

Comparison of equation (30) with (16) allows identification of the Lagrange parameters  $\lambda_1 = \beta$ ,  $\lambda_2 = \pi$  and  $\lambda_3 = \nu$  and to obtain:

$$\sum_{i \in \Omega} e^{-(\beta E_i + \pi V_i + \nu N_i)} = 1. \quad (31)$$

Thus, from (29), the probabilities of the microstates in the Generalized Ensemble are:

$$p_i = e^{-(\beta E_i + \pi V_i + \nu N_i)} \quad \forall i \in \Omega. \quad (32)$$

Note that these  $p_i$  already satisfy the normalization condition (31). This is a consequence of the Gibbs-Duhem equation (23) [17].

## IV. RESTRICTED STATISTICAL ENSEMBLES

### A. Microcanonical Ensemble

In the Microcanonical Ensemble the energy  $E$ , volume  $V$  and number of particles  $N$  are fixed. We consider the subset  $\Omega_{E,V,N} \subset \Omega$  ( $\forall i \in \Omega_{E,V,N}$ ,  $E_i = E$ ,  $V_i = V$  and  $N_i = N$ ). By imposing this condition on equation (32), we obtain:

$$p_i = e^{-(\beta E + \pi V + \nu N)}, \quad (33)$$

which is independent of the state of the system. From the normalization condition (31) we obtain:

$$\mathcal{Q}_M e^{-(\beta E + \pi V + \nu N)} = 1, \quad (34)$$

where  $\mathcal{Q}_M$  is the Microcanonical partition function or number of available microstates (we have denoted it by  $\mathcal{W}$  in the introduction). Taking into account (16), we recover the characteristic equation of the Microcanonical Ensemble:

$$\mathcal{S}(E, V, N) = \ln \mathcal{Q}_M. \quad (35)$$

### B. Canonical Ensemble

In this case the volume and the number of particles are fixed, while energy, which is controlled by the temperature of a reservoir in thermal contact with the system, can fluctuate. Therefore from (31):

$$e^{-(\pi V + \nu N)} \sum_{i \in \Omega_{V,N}} e^{-\beta E_i} = 1. \quad (36)$$

From (9) and (16), it results that:

$$\Phi = \pi V + \nu N \quad (37)$$

and thus:

$$\Phi(\beta, V, N) = \ln \mathcal{Q}_C \quad (38)$$

where:

$$\mathcal{Q}_C = \sum_{i \in \Omega_{V,N}} e^{-\beta E_i} \quad (39)$$

is the Canonical partition function.

### C. Grand Canonical Ensemble

The situation is similar, but now, compared to the Canonical case, the number of particles can also fluctuate, controlled by the chemical potential of the reservoir. Following the same procedure as before we obtain:

$$\Psi(\beta, V, \nu) = \ln \mathcal{Q}_{GC} \quad (40)$$

where the Grand Canonical partition function  $\mathcal{Q}_{GC}$  is given by:

$$\mathcal{Q}_{GC} = \sum_{i \in \Omega_V} e^{-(\beta E_i + \nu N_i)}. \quad (41)$$

### D. Other Statistical Ensembles

Let us now consider a system with  $\mathcal{N}$  degrees of freedom and the ensemble of microstates for which  $n$  extensive variables have been fixed  $\Omega_{X_1, \dots, X_n}$ . Taking into account the preceding examples it is clear that, within the entropic formulation, the characteristic equation takes the general form:

$$\psi(X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}) = \ln \mathcal{Q}, \quad (42)$$

where  $\psi(X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}})$  is the corresponding Massieu-Planck function obtained after a Legendre transformation of the entropy with respect to the variables  $X_{n+1}, \dots, X_{\mathcal{N}}$  and  $\mathcal{Q}$  is the partition function of this generic ensemble.

For this ensemble we develop the corresponding formulas for the averages and fluctuations of extensive variables. The averages of the fluctuating extensive variables are obtained from:

$$\langle X_k \rangle = -\frac{\partial \ln \mathcal{Q}}{\partial y_k} \quad k = n + 1, \dots, \mathcal{N}, \quad (43)$$

whereas the intensive variables conjugated from the fixed extensive variables satisfy:

$$y_k = \frac{\partial \ln \mathcal{Q}}{\partial X_k} \quad k = 1, \dots, n. \quad (44)$$

It is worth noting that these last derivatives can be expressed in terms of average values of microscopic generalized forces  $\langle \frac{\partial X_k}{\partial X_l} \rangle$  with  $k = n + 1, \dots, \mathcal{N}$  and  $l = 1, \dots, n$  [13]. For instance, for a pure substance under hydrostatic conditions, the microscopic quantity related to  $\pi$  is  $\beta \frac{\partial E_i}{\partial V}$ , and the microscopic quantity related to  $\nu$  is  $\beta \frac{\partial E_i}{\partial N}$ .

The covariance matrix of the extensive fluctuating variables is easily obtained as:

$$\langle X_k X_l \rangle - \langle X_k \rangle \langle X_l \rangle = \frac{\partial^2 \ln \mathcal{Q}}{\partial y_k \partial y_l} \quad \forall k, l = n + 1, \dots, \mathcal{N}. \quad (45)$$

The diagonal elements correspond to the variances (fluctuations) of the extensive variables:

$$\langle X_k^2 \rangle - \langle X_k \rangle^2 = \frac{\partial^2 \ln \mathcal{Q}}{\partial y_k^2} = \frac{\partial \langle X_k \rangle}{\partial y_k} \quad \forall k = n + 1, \dots, \mathcal{N}. \quad (46)$$

The last terms in these equalities are response functions. Therefore, these equations (46) correspond to the fluctuation-dissipation theorem.

## V. EXAMPLES

Let us discuss two examples of application of the new proposed formalism, to show its advantages:

### A. Example 1: average values and fluctuations of $E$ and $N$ in the Grand Canonical Ensemble

Classical textbooks have presented this case in many different ways. In the standard Grand Canonical formulation for an hydrostatic pure substance one selects  $T$ ,  $V$  and  $\mu$  as

independent variables so that the corresponding energetic potential is  $\Theta = -pV$  and the basic equation reads [6]:

$$\Theta(T, V, \mu) \equiv -pV = -kT \ln Q_{GC} \quad (47)$$

with

$$Q_{GC}(T, V, \mu) = \sum_{\Omega_V} e^{-E_i/kT + \mu N_i/kT}. \quad (48)$$

In terms of  $T$ ,  $V$  and  $\mu$ , the expressions giving the average number of particles and energy are:

$$\langle N \rangle = - \left( \frac{\partial \Theta}{\partial \mu} \right)_{V, T} \quad (49)$$

and

$$U \equiv \langle E \rangle = -\mu \left( \frac{\partial \Theta}{\partial \mu} \right)_{T, V} - T \left( \frac{\partial \Theta}{\partial T} \right)_{\mu, V} + \Theta. \quad (50)$$

The fluctuations of these quantities are:

$$\langle E^2 \rangle - \langle E \rangle^2 = -kT^3 \left( \frac{\partial^2 \Theta}{\partial T^2} \right)_{\mu, V} - kT \mu^2 \left( \frac{\partial^2 \Theta}{\partial \mu^2} \right)_{T, V} \quad (51)$$

$$\langle N^2 \rangle - \langle N \rangle^2 = -kT \left( \frac{\partial^2 \Theta}{\partial \mu^2} \right)_{T, V}. \quad (52)$$

Actually, the above formulas (49)-(52) are not usually written in such a form in a standard textbook. Instead, different changes of variables are proposed in order to simplify them. For instance, in the first edition of Pathria's book [6], the fugacity  $z = e^{\mu/kT}$  is introduced. In the second edition, different strategies ( $z$  or  $-\mu/kT$ ) are adopted when developing the thermodynamics of the ensemble. In our context the choice of the variables is already clear. They directly follow from Eq. 40. Average values of the energy and number of particles are computed, within this framework, as

$$U \equiv \langle E \rangle = - \left( \frac{\partial \Psi}{\partial \beta} \right)_{V, \nu} \quad \langle N \rangle = - \left( \frac{\partial \Psi}{\partial \nu} \right)_{\beta, V} \quad (53)$$

and fluctuations are simply given by :

$$\langle E^2 \rangle - \langle E \rangle^2 = \left( \frac{\partial^2 \Psi}{\partial \beta^2} \right)_{\nu, V} = - \left( \frac{\partial U}{\partial \beta} \right)_{\nu, V} \quad (54)$$

$$\langle N^2 \rangle - \langle N \rangle^2 = \left( \frac{\partial^2 \Psi}{\partial \nu^2} \right)_{\beta, V} = - \left( \frac{\partial \langle N \rangle}{\partial \nu} \right)_{\beta, V} . \quad (55)$$

Moreover, these variables,  $E$  and  $N$ , are not independent in the Grand Canonical Ensemble. It is straightforward to compute their covariance, which is a quantity that is usually not analyzed in textbooks:

$$\langle NE \rangle - \langle N \rangle \langle E \rangle = \left( \frac{\partial}{\partial \nu} \left( \frac{\partial \Psi}{\partial \beta} \right)_{\nu, V} \right)_{\beta, V} = - \left( \frac{\partial U}{\partial \nu} \right)_{\beta, V} = - \left( \frac{\partial \langle N \rangle}{\partial \beta} \right)_{\nu, V} . \quad (56)$$

The last equality corresponds to a Maxwell relation. It is interesting to compare, within the present framework, the energy fluctuations in this Grand Canonical ensemble to those in the Canonical ensemble whose variance is given by:

$$\langle E^2 \rangle_C - \langle E \rangle_C^2 = \left( \frac{\partial^2 \Phi}{\partial \beta^2} \right)_{N, V} = - \left( \frac{\partial U}{\partial \beta} \right)_{N, V} = k\beta^2 C_V, \quad (57)$$

where  $C_V$  is the constant volume heat capacity. The relation between the derivative  $\left( \frac{\partial U}{\partial \beta} \right)_{N, V}$  and  $\left( \frac{\partial U}{\partial \beta} \right)_{\nu, V}$  (appearing in equation 54) is:

$$\begin{aligned} \left( \frac{\partial U}{\partial \beta} \right)_{\nu, V} &= \left( \frac{\partial U}{\partial \beta} \right)_{N, V} + \left( \frac{\partial U}{\partial N} \right)_{\beta, V} \left( \frac{\partial N}{\partial \beta} \right)_{\nu, V} = \\ &= \left( \frac{\partial U}{\partial \beta} \right)_{N, V} + \left( \frac{\partial U}{\partial \nu} \right)_{\beta, V} \left( \frac{\partial \nu}{\partial N} \right)_{\beta, V} \left( \frac{\partial N}{\partial \beta} \right)_{\nu, V} . \end{aligned} \quad (58)$$

Taking into account equations (55) and (56) one easily obtains [18]:

$$\langle E^2 \rangle - \langle E \rangle^2 = \left( \langle E^2 \rangle_C - \langle E \rangle_C^2 \right) + \frac{[\langle NE \rangle - \langle N \rangle \langle E \rangle]^2}{\langle N^2 \rangle - \langle N \rangle^2}, \quad (59)$$

where all the average values refer to the Grand Canonical Ensemble except those indicated by  $\langle \dots \rangle_C$  which correspond to Canonical averages. By taking into account the definition of statistical correlation ( $corr(N, E)$ ) between two random variables, equation (59) can be transformed into:

$$\langle E^2 \rangle_C - \langle E \rangle_C^2 = \left( \langle E^2 \rangle - \langle E \rangle^2 \right) \left[ 1 - corr^2(N, E) \right]. \quad (60)$$

## B. Example 2: the magnetic solid

The magnetic solid is another interesting system to be discussed within the present formulation. As usual, let us consider that the magnetic moments  $\vec{m}$  are all identical, localized on a rigid lattice (ignoring pressure effects), and that only their component along the external magnetic field  $\vec{H}$  are relevant. The microstates  $i$  of the crystal are characterized by the energy  $E_i$ , the total magnetization in the direction of the field  $M_i$  and the total number of magnetic moments  $N_i$ . Note that in any state  $i$ :

$$M_i = \sum_{k=1}^{N_i} m_{ki}, \quad (61)$$

where the sum extends over all lattice sites and  $m_{ki}$  is the projection of  $\vec{m}_k$  along the field  $\vec{H}$ .

Some textbooks (see, for example [6] and [12]) include a treatment of such a system within the Canonical ensemble and obtain a “Hemholtz free energy”  $F(T, H, N)$ . Such a treatment, from our own teaching experience, is somewhat confusing to students. Within the Canonical Ensemble the adequate choice should be  $T$ ,  $M$  (magnetization) and  $N$ . The choice of  $T$ ,  $H$  and  $N$  as independent variables corresponds to the Isofield-Isothermal ensemble. For such a system the fundamental thermodynamic equation reads:

$$d\mathcal{S} = \beta dU - h dM - \nu dN, \quad (62)$$

where  $h = H/kT$ . The suitable Massieu-Planck function in our formalism is the magnetic version of the Planck potential:

$$\Xi_{mag}(\beta, h, N) = \mathcal{S} - \beta U + hM. \quad (63)$$

The statistical mechanics of this ensemble is obtained from equation:

$$\Xi_{mag} = \ln \mathcal{Q}^H, \quad (64)$$

where

$$Q^{II} = \sum_{i \in \Omega_N} e^{-\beta E_i - h M_i}. \quad (65)$$

If we assume now that the magnetic moments are not interacting,  $E_i = \sum_{k=1}^N e_{ki}$ , where  $e_j$  are the individual energy levels of the magnetic moments. The partition function can be written as:

$$Q^{II} = q^N, \quad (66)$$

where

$$q = \sum_{j \in \omega} e^{-\beta e_j - h m_j} \quad (67)$$

and  $\omega$  is the set of states of an individual magnetic moment. Moreover, if we assume that the magnetic moments are structureless and practically static, then only an energy level is available  $e_j = e_0$ . By choosing the origin of energies so that  $e_0 = 0$ , the partition function can be written as:

$$Q^{II} = \left[ \sum_{j \in \omega} e^{-h m_j} \right]^N. \quad (68)$$

Consequently, the only variable playing a role in this problem is  $h = H/kT$ . All the thermodynamic quantities will, therefore, scale with  $H/kT$ .

Finally, it is interesting to note that in this paramagnetic case  $U = 0$  and thus,  $\Xi_{mag} = \mathcal{S} + hM$ . Therefore, the suitable choice of Massieu-Planck function is  $\Lambda_{mag}(E = 0, h, N)$ . In the ferromagnetic case, however, due to the existence of interactions,  $\Xi_{mag}(\beta, h, N)$  must be used.

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- [18] This result corresponds to formula 4.5.14 together with the result of problem 4.12 in Pathria’s textbook (new edition).