

Entropic Formulation of Statistical Mechanics

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We present an alternative formulation of Equilibrium Statistical Mechanics which 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 of the equations that relate the average values with derivatives of the partition function are formally identical in the different ensembles. Moreover, Einstein’s fluctuation formula is also derived within the same framework. This provides a suitable starting point for the calculation of fluctuations of extensive and intensive variables in any statistical ensemble.

KEY WORDS: Equilibrium Statistical Mechanics; Information Theory; Maximum Statistical Entropy Principle; Massieu–Planck functions; Einstein’s fluctuations.

1. 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 :

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

This formulation, proposed by Jaynes,⁽¹⁾ is based on the so-called Maximum Statistical Entropy Principle within the context of Information Theory.^(2, 3) The thermodynamic entropy S is a quantity defined for equilibrium (macro) states of a system. On the other hand, the statistical entropy functional

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$\hat{\mathcal{S}}(\{p_i\})$ characterizes the uncertainty associated with any mathematically well-defined ($0 \leq p_i \leq 1$ and $\sum_{i \in \Omega} p_i = 1$) probability distribution $\{p_i\}$ on the set of available microstates $\Omega = \{i\}$.

The functional $\hat{\mathcal{S}}(\{p_i\})$ is required to satisfy the two following general properties: (i) $\hat{\mathcal{S}}$ must be positive, taking 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. In addition, if we require the condition that (iii) $\hat{\mathcal{S}}$ is additive for independent sources of uncertainty, then it can be demonstrated⁽⁴⁾ that the functional $\hat{\mathcal{S}}$ has the following form:

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

A direct consequence of the latter requirement (iii) is the property of extensivity, which can be formulated as follows; let us consider a system composed of two independent subsystems A and B so that the set of microstates is $\Omega_{A+B} = \Omega_A \times \Omega_B$. Each microstate (i, j) can be specified by fixing a state $i \in \Omega_A$ of the subsystem A and a state $j \in \Omega_B$ of the subsystem B . If a probability density $p_{(i,j)}^{A+B}$ satisfies $p_{(i,j)}^{A+B} = p_i^A p_j^B$ then $\hat{\mathcal{S}}^{A+B} = \hat{\mathcal{S}}^A + \hat{\mathcal{S}}^B$.

Let us consider 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, Eq. (1) reduces to the well-known equation proposed by Boltzmann in 1877:⁽⁵⁾

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

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 allowed 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 $\Omega_{V,N} \supset \Omega_{E,V,N}$.⁽⁶⁾ 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 :^(7, 8)

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

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 and mean number of particles. 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 to 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 Eqs. (3) and (4). Therefore, all the equations derived for the average values and fluctuations of different microscopic quantities are also formally different.

The aim of the present paper is to show that if the different statistical ensembles are constructed by choosing appropriate variables, the thermodynamic-statistical connection can be established using an entropic potential through a basic equation formally identical to Eq. (3) for all the different ensembles. As will be shown, the relevant thermodynamic potentials in this case are Massieu–Planck functions⁽⁹⁾ obtained by means of Legendre transformations of the entropy. Actually, the interest in Massieu–Planck functions in Statistical Mechanics has already been mentioned in Callen’s book.⁽¹⁰⁾ However, standard formulations of Statistical Physics^(3, 7, 8, 11–13) do not make use of them at all. Exceptions are found in Balian’s and Münster’s books,^(3, 14) where the formal treatment of Generalized Ensembles is based on Massieu–Planck functions, with viewpoints that share 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 that determine 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 2 Massieu–Planck functions are introduced. In Section 3 the Ensemble Theory is formulated by making use of the previously introduced natural thermodynamic variables for Massieu–Planck functions. In Section 4 Einstein’s formula for the probability of fluctuations is derived within the context of the Information Theory. Finally, in Section 5 such a formula is applied to the study of the fluctuations of intensive and extensive variables in the different equilibrium statistical ensembles.

2. THERMODYNAMICS: ENTROPIC VARIABLES AND MASSIEU-PLANCK FUNCTIONS

For the sake of clarity, 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 μ are the temperature, the pressure and the chemical potential.

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, we have:

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

where X_k are extensive variables, and y_k are the corresponding entropic conjugate variables. Massieu-Planck functions⁽⁹⁾ 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:

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

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

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

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

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

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

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

The function Φ was first introduced by Massieu,⁽¹⁵⁾ and is called Massieu's potential. The function Ξ was introduced by Planck⁽¹⁶⁾ and is called Planck's potential. The extensivity of \mathcal{S} implies the following scaling property when the complete set of natural variables U , V , and N are re-scaled by a factor λ :

$$\mathcal{S}(\lambda U, \lambda V, \lambda N) = \lambda \mathcal{S}(U, V, N). \quad (16)$$

Euler's theorem for homogeneous functions enables the following equation to be obtained:

$$\mathcal{S} = \beta U + \pi V + \nu N, \quad (17)$$

that is, the Legendre transformation of all the variables redefines the entropy and, therefore $\Pi = 0$. Substituting Eq. (7) into the differentials of the potentials defined above, we obtain:

$$d\Phi = -U d\beta + \pi dV + \nu dN \quad (18)$$

$$d\Lambda = \beta dU - V d\pi + \nu dN \quad (19)$$

$$d\Gamma = \beta dU + \pi dV - N d\nu \quad (20)$$

$$d\Xi = -U d\beta - V d\pi + \nu dN \quad (21)$$

$$dY = \beta dU - V d\pi - N d\nu \quad (22)$$

$$d\Psi = -U d\beta + \pi dV - N d\nu, \quad (23)$$

and from Eq. (17) one obtains:

$$U d\beta + V d\pi + N d\nu = 0. \quad (24)$$

The above equations allow a re-derivation of all the standard thermodynamic equations in terms of β , π , and ν . For instance, Maxwell relations can be easily deduced, by imposing that the Eqs. (18)–(23) are exact differentials (equality of crossed derivatives). Moreover, Eq. (24) 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} allows us to deduce that β , π , and ν are homogeneous at equilibrium.⁽¹⁷⁾

3. GIBBS-BOLTZMANN STATISTICAL MECHANICS

3.1. Generalized Ensemble

In contrast to usual procedures, the statistical ensembles will be introduced here by starting with the most generalized ensemble (a completely open system) and later imposing the constraints that lead to the standard ensembles. Thus, we begin by studying what we call the Generalized Ensemble in which the system can exchange energy, volume and particles with the surroundings, but keeps the corresponding average values of E , V , and N constant:

$$U \equiv \langle E \rangle = \sum_{i \in \Omega} p_i E_i, \quad (25)$$

$$\langle V \rangle = \sum_{i \in \Omega} p_i V_i, \quad (26)$$

$$\langle N \rangle = \sum_{i \in \Omega} p_i N_i. \quad (27)$$

Using the method of Lagrange multipliers we maximize the statistical entropy functional subject to the constraints (25)–(27) and the normalization condition of the probabilities p_i . This gives:

$$\frac{\partial \mathcal{L}}{\partial p_i} = 0, \quad (28)$$

where:

$$\mathcal{L}(\{p_i\}) = - \sum_{i \in \Omega} p_i \ln p_i - \lambda_0 \sum_{i \in \Omega} p_i - \lambda_1 \sum_{i \in \Omega} E_i p_i - \lambda_2 \sum_{i \in \Omega} V_i p_i - \lambda_3 \sum_{i \in \Omega} N_i p_i. \quad (29)$$

Note that, in this ensemble, Ω 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:

$$p_i = \frac{e^{-(\lambda_1 E_i + \lambda_2 V_i + \lambda_3 N_i)}}{\sum_{i \in \Omega} e^{-(\lambda_1 E_i + \lambda_2 V_i + \lambda_3 N_i)}}. \quad (30)$$

The value of the entropy at the maximum is:

$$\mathcal{S} = \left(\ln \sum_{i \in \Omega} e^{-(\lambda_1 E_i + \lambda_2 V_i + \lambda_3 N_i)} \right) + \lambda_1 U + \lambda_2 \langle V \rangle + \lambda_3 \langle N \rangle. \quad (31)$$

Comparison of Eq. (31) with Eq. (17) allows identification of the Lagrange parameters $\lambda_1 = \beta$, $\lambda_2 = \pi$ and $\lambda_3 = \nu$ and the following expression to be obtained:

$$\sum_{i \in \Omega} e^{-(\beta E_i + \pi V_i + \nu N_i)} = 1. \quad (32)$$

Thus, from (30), the probabilities of the microstates in the Generalized Ensemble are:

$$p_i = e^{-(\beta E_i + \pi V_i + \nu N_i)}, \quad \forall i \in \Omega. \quad (33)$$

Note that these p_i already satisfy the normalization condition (32). This is a consequence of the Gibbs–Duhem equation (24).⁽¹⁸⁾

In the following subsections we develop different restricted statistical ensembles and consider a number of examples.

3.2. 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 Eq. (33), we obtain:

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

which is independent of the state of the system. From the normalization condition (32) we obtain:

$$\mathcal{Q}_M e^{-(\beta E + \pi V + \nu N)} = 1, \quad (35)$$

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 (17), we recover the characteristic equation of the Microcanonical Ensemble:

$$\mathcal{S}(E, V, N) = \ln \mathcal{Q}_M. \quad (36)$$

3.3. Canonical Ensemble

In this case the volume and the number of particles are fixed, while the energy, which is controlled by the temperature of a reservoir in thermal contact with the system, can fluctuate. Therefore, from (32):

$$e^{-(\pi V + \nu N)} \sum_{i \in \Omega_{V, N}} e^{-\beta E_i} = 1. \quad (37)$$

From (9) and (17), it is seen that:

$$\Phi = \pi V + \nu N \quad (38)$$

and thus:

$$\Phi(\beta, V, N) = \ln \mathcal{Q}_C \quad (39)$$

where:

$$\mathcal{Q}_C = \sum_{i \in \Omega_{V,N}} e^{-\beta E_i} \quad (40)$$

is the Canonical partition function.

3.4. Grand Canonical Ensemble

The situation is similar, however now, in comparison with 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:

$$\Psi(\beta, V, \nu) = \ln \mathcal{Q}_{GC} \quad (41)$$

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

$$\mathcal{Q}_{GC} = \sum_{i \in \Omega_V} e^{-(\beta E_i + \nu N_i)}. \quad (42)$$

3.5. Other Statistical Ensembles

Let us now consider a generic system with \mathcal{N} degrees of freedom and the ensemble of microstates for which n ($n \leq \mathcal{N}$) extensive variables have been fixed Ω_{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:

$$\psi(X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}) = \ln \mathcal{Q}, \quad (43)$$

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 $X_{n+1}, \dots, X_{\mathcal{N}}$ ($\psi = \mathcal{S} - \sum_{k=n+1}^{\mathcal{N}} y_k X_k$) and \mathcal{Q} is the partition function of this generic ensemble.

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

$$\langle X_k \rangle = -\frac{\partial \ln \mathcal{Q}}{\partial y_k}, \quad k = n+1, \dots, \mathcal{N}, \quad (44)$$

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

$$y_k = \frac{\partial \ln \mathcal{Q}}{\partial X_k}, \quad k = 1, \dots, n. \quad (45)$$

It is worth noting that these latter derivatives can be expressed in terms of average values of microscopic generalized forces $\frac{\partial X_k}{\partial X_l}$ with $k = n+1, \dots, \mathcal{N}$ and $l = 1, \dots, n$.⁽¹⁴⁾ For instance, for a pure substance under hydrostatic conditions, the microscopic quantity related to π is $\beta \frac{\partial E_i}{\partial V}$, and the microscopic quantity related to ν is $\beta \frac{\partial E_i}{\partial N}$.

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

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

where we have defined $\Delta X_k = X_k - \langle X_k \rangle$. The diagonal elements correspond to the variances (commonly called fluctuations) of the extensive variables:

$$\langle \Delta X_k^2 \rangle = \frac{\partial^2 \ln \mathcal{Q}}{\partial y_k^2} = -\frac{\partial \langle X_k \rangle}{\partial y_k}, \quad \forall k = n+1, \dots, \mathcal{N}. \quad (47)$$

The latter terms in these equalities are response functions. Therefore, these Eqs. (47) correspond to the (static) fluctuation-dissipation relations.

In the next three sections examples of the application of the above formalism to specific ensembles are presented.

3.6. Example 1: Grand Canonical Fluctuations

As a first example, we consider the calculation of the fluctuations in the Grand Canonical ensemble. In order to illustrate the advantages of the proposed formalism, we first carry out the calculation within the standard Statistical Mechanics framework.

For an hydrostatic pure substance T , V , and μ are selected as independent variables so that the corresponding energetic potential is $\Theta = -pV$ and the basic equation reads:⁽⁷⁾

$$\Theta(T, V, \mu) \equiv -pV = -kT \ln \mathcal{Q}_{GC} \quad (48)$$

with

$$\mathcal{Q}_{GC}(T, V, \mu) = \sum_{\Omega_V} e^{-E_i/kT + \mu N_i/kT}. \quad (49)$$

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

$$\langle N \rangle = - \left(\frac{\partial \Theta}{\partial \mu} \right)_{V, T} \quad (50)$$

and

$$U \equiv \langle E \rangle = -\mu \left(\frac{\partial \Theta}{\partial \mu} \right)_{T, V} - T \left(\frac{\partial \Theta}{\partial T} \right)_{\mu, V} + \Theta. \quad (51)$$

The fluctuations of these quantities are:

$$\langle \Delta E^2 \rangle = -kT^3 \left(\frac{\partial^2 \Theta}{\partial T^2} \right)_{\mu, V} - kT \mu^2 \left(\frac{\partial^2 \Theta}{\partial \mu^2} \right)_{T, V} \quad (52)$$

$$\langle \Delta N^2 \rangle = -kT \left(\frac{\partial^2 \Theta}{\partial \mu^2} \right)_{T, V}. \quad (53)$$

Actually, the above formulas (50)–(53) are not usually written as shown above in standard textbooks. Instead, different changes of variables are proposed in order to simplify them. For instance, in the first edition of Pathria's book,⁽⁷⁾ the fugacity $z = e^{\mu/kT}$ is introduced. In the second edition, different strategies (either using 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. (41). Average values of the energy and number of particles are computed, within this framework, as

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

and fluctuations are simply given by:

$$\langle \Delta E^2 \rangle = \left(\frac{\partial^2 \Psi}{\partial \beta^2} \right)_{v,V} = - \left(\frac{\partial U}{\partial \beta} \right)_{v,V} \quad (55)$$

$$\langle \Delta N^2 \rangle = \left(\frac{\partial^2 \Psi}{\partial v^2} \right)_{\beta,V} = - \left(\frac{\partial \langle N \rangle}{\partial v} \right)_{\beta,V}. \quad (56)$$

Moreover, the fluctuations of E and N , are not independent in the Grand Canonical Ensemble. It is straightforward to compute their covariance:

$$\langle \Delta E \Delta N \rangle = \left(\frac{\partial}{\partial v} \left(\frac{\partial \Psi}{\partial \beta} \right)_{v,v} \right)_{\beta,V} = - \left(\frac{\partial U}{\partial v} \right)_{\beta,V} = - \left(\frac{\partial \langle N \rangle}{\partial \beta} \right)_{v,V}. \quad (57)$$

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

$$\langle \Delta E^2 \rangle_C = \left(\frac{\partial^2 \Phi}{\partial \beta^2} \right)_{N,V} = - \left(\frac{\partial U}{\partial \beta} \right)_{N,V} = k\beta^2 C_V, \quad (58)$$

where C_V is the constant volume heat capacity. The relation between the derivative $\left(\frac{\partial U}{\partial \beta} \right)_{N,V}$ and $\left(\frac{\partial U}{\partial \beta} \right)_{v,V}$ [appearing in Eq. (55)] is:

$$\begin{aligned} \left(\frac{\partial U}{\partial \beta} \right)_{v,V} &= \left(\frac{\partial U}{\partial \beta} \right)_{N,V} + \left(\frac{\partial U}{\partial N} \right)_{\beta,V} \left(\frac{\partial N}{\partial \beta} \right)_{v,V} \\ &= \left(\frac{\partial U}{\partial \beta} \right)_{N,V} + \left(\frac{\partial U}{\partial v} \right)_{\beta,V} \left(\frac{\partial v}{\partial N} \right)_{\beta,V} \left(\frac{\partial N}{\partial \beta} \right)_{v,V}. \end{aligned} \quad (59)$$

Taking into account Eqs. (56) and (57) one easily obtains:

$$\langle \Delta E^2 \rangle = \langle \Delta E^2 \rangle_C + \frac{\langle \Delta E \Delta N \rangle^2}{\langle \Delta N^2 \rangle}, \quad (60)$$

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 ($\rho(N, E)$) between two random variables, Eq. (60) can be transformed into:

$$\langle \Delta E^2 \rangle_C = \langle \Delta E^2 \rangle (1 - \rho(N, E)^2). \quad (61)$$

3.7. Example 2: The Isothermal–Isobaric Ensemble

Another particular example of interest is that of a system with a fixed number of particles, but that has energy and volume fluctuations. Although this case corresponds to typical experimental situations, it is not frequently studied. The connexion between thermodynamics and statistical mechanics, in this case is established through:

$$\mathcal{E}(\beta, \pi, N) = \ln \mathcal{Q}_{IB} \quad (62)$$

with

$$\mathcal{Q}_{IB} = \sum_{i \in \Omega_N} e^{-(\beta E_i + \pi V_i)}. \quad (63)$$

Following the same strategy as in the Grand Canonical ensemble we easily obtain:

$$U \equiv \langle E \rangle = -\left(\frac{\partial \mathcal{E}}{\partial \beta}\right)_{\pi, N}, \quad \langle V \rangle = -\left(\frac{\partial \mathcal{E}}{\partial \pi}\right)_{\beta, N} \quad (64)$$

and the energy and volume fluctuations are simply given by:

$$\langle \Delta E^2 \rangle = \left(\frac{\partial^2 \mathcal{E}}{\partial \beta^2}\right)_{\pi, N} = -\left(\frac{\partial U}{\partial \beta}\right)_{\pi, N}, \quad (65)$$

$$\langle \Delta V^2 \rangle = \left(\frac{\partial^2 \mathcal{E}}{\partial \pi^2}\right)_{\beta, N} = -\left(\frac{\partial \langle V \rangle}{\partial \pi}\right)_{\beta, N}, \quad (66)$$

and their covariance is:

$$\langle \Delta E \Delta V \rangle = \left(\frac{\partial}{\partial \pi} \left(\frac{\partial \mathcal{E}}{\partial \beta}\right)_{N, \pi}\right)_{\beta, N} = -\left(\frac{\partial U}{\partial \pi}\right)_{\beta, N} = -\left(\frac{\partial \langle V \rangle}{\partial \beta}\right)_{\pi, N}. \quad (67)$$

Energy fluctuations in this ensemble are related to canonical energy fluctuations through the expression:

$$\langle \Delta E^2 \rangle = \langle \Delta E^2 \rangle_c + \frac{\langle \Delta E \Delta V \rangle^2}{\langle \Delta V^2 \rangle}. \quad (68)$$

3.8. Example 3: The Magnetic Solid

The magnetic solid is another interesting system that can 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 :

$$M_i = \sum_{k=1}^{N_i} m_{ki}, \quad (69)$$

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, refs. 7 and 13) include a treatment of such a system within the Canonical ensemble and obtain a ‘‘Hemholtz free energy’’ $F(T, H, N)$. Such a treatment, is somewhat confusing. 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 Isothermal–Isofield ensemble. For such a system the fundamental thermodynamic equation reads:

$$d\mathcal{S} = \beta dU - h dM + v dN, \quad (70)$$

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

$$\mathcal{E}_{\text{mag}}(\beta, h, N) = \mathcal{S} - \beta U + hM. \quad (71)$$

The statistical mechanics of this ensemble is obtained from equation:

$$\mathcal{E}_{\text{mag}} = \ln \mathcal{Q}_{IF}, \quad (72)$$

where

$$\mathcal{Q}_{IF} = \sum_{i \in \Omega_N} e^{-\beta E_i + hM_i}. \quad (73)$$

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

$$\mathcal{Q}_{IF} = q^N, \quad (74)$$

where

$$q = \sum_{j \in \omega} e^{-\beta e_j + hm_j} \quad (75)$$

and ω 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 a single 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:

$$\mathcal{Q}_{IF} = \left[\sum_{j \in \omega} e^{+hm_j} \right]^N. \quad (76)$$

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, $\mathcal{E}_{\text{mag}} = \mathcal{S} + hM$. Therefore, another suitable choice of Massieu–Planck function is $A_{\text{mag}}(E = 0, h, N)$. In the ferromagnetic case, however, due to the existence of interactions, $\mathcal{E}_{\text{mag}}(\beta, h, N)$ must be used.

4. GENERAL THEORY OF FLUCTUATIONS

In this section we derive Einstein's formula for the probability of fluctuations around the equilibrium state to occur. The derivation method, based on Information Theory, is similar to that proposed recently in ref. 19. Let us consider a system with a set of microstates $\Omega = \{i\}$ for which the equilibrium distribution which maximizes the statistical entropy is $\{p_i(0)\}$. A virtual displacement of this system from the initial equilibrium situation can be understood as the change of an adjustable internal constraint that enables the distribution $\{p_i(0)\}$ to be modified. Let us characterize such a displacement by a (multidimensional) continuous parameter κ which takes values over a certain range \mathcal{R} . The set of functions $\{p_i(\kappa)\}$ represents the constrained equilibrium probability distributions given a certain value of κ . We define κ such that for the initial equilibrium situation, $\kappa = 0$.

Each of these probability distributions $\{p_i(\kappa)\}$ corresponds to the distribution with maximum statistical entropy for a given value of κ and satisfies the normalization condition over Ω .

$$\sum_{i \in \Omega} p_i(\kappa) = 1. \quad (77)$$

Now we consider κ itself as a random variable which accounts for how far the system fluctuates from the equilibrium distribution $\{p_i(0)\}$. Our aim

is to find the density probability law $p(\kappa)$ for the parameter κ . Since $\{p_i(\kappa)\}$ is the conditional probability for each state i given κ , the joint probability $p(i, \kappa)$ (defined on $\Omega \times \mathcal{R}$) satisfies:

$$p(i, \kappa) = p(\kappa) p_i(\kappa) \quad (78)$$

Following the same strategy as above for the determination of the probability densities for each statistical ensemble, we apply the Maximum Statistical Entropy Principle in order to determine $p(\kappa)$. The statistical entropy, associated with the joint probability $\{p(i, \kappa)\}$, which must be maximized is:

$$\hat{\mathcal{S}}(\{p(i, \kappa)\}) = - \int_{\mathcal{R}} d\kappa \sum_{i \in \Omega} p(i, \kappa) \ln p(i, \kappa). \quad (79)$$

By introducing Eq. (78) into this expression, it can be written in terms of $p(\kappa)$, which is the adjustable function for the maximization. This gives:

$$\hat{\mathcal{S}}(p(\kappa)) = - \int_{\mathcal{R}} d\kappa \sum_{i \in \Omega} p(\kappa) p_i(\kappa) \ln p(\kappa) p_i(\kappa), \quad (80)$$

and taking into account (77) we obtain:

$$\hat{\mathcal{S}}(p(\kappa)) = - \int_{\mathcal{R}} d\kappa p(\kappa) \ln p(\kappa) - \int_{\mathcal{R}} d\kappa p(\kappa) \sum_{i \in \Omega} p_i(\kappa) \ln p_i(\kappa). \quad (81)$$

Note that the sum in the second term is the statistical entropy of the distribution $p_i(\kappa)$, which is nothing more than the entropy of the virtually displaced system. Let us call it $\mathcal{S}(\kappa)$. Thus,

$$\hat{\mathcal{S}}(p(\kappa)) = - \int_{\mathcal{R}} d\kappa p(\kappa) \ln p(\kappa) - \int_{\mathcal{R}} d\kappa p(\kappa) \mathcal{S}(\kappa). \quad (82)$$

The maximization of this expression with respect to the function $p(\kappa)$ must be performed under the normalization condition:

$$\int_{\mathcal{R}} d\kappa p(\kappa) = 1. \quad (83)$$

We proceed as in Section 3 defining:

$$\mathcal{L}[p(\kappa)] = - \int_{\mathcal{R}} d\kappa p(\kappa) \ln p(\kappa) - \int_{\mathcal{R}} d\kappa p(\kappa) \mathcal{S}(\kappa) - \lambda \int_{\mathcal{R}} d\kappa p(\kappa). \quad (84)$$

From the extremal condition:

$$\frac{\delta \mathcal{L}}{\delta p(\kappa)} = 0, \quad (85)$$

we easily obtain $-\mathcal{S}(\kappa) - \ln p(\kappa) - 1 - \lambda = 0$, where λ is determined from the normalization condition (83). The final expression for $p(\kappa)$ is:

$$p(\kappa) = \frac{e^{\mathcal{S}(\kappa)}}{\int_{\mathcal{R}} d\kappa e^{\mathcal{S}(\kappa)}} = \frac{e^{\mathcal{S}(\kappa) - \mathcal{S}(0)}}{\int_{\mathcal{R}} d\kappa e^{\mathcal{S}(\kappa) - \mathcal{S}(0)}} \propto e^{\mathcal{S}(\kappa) - \mathcal{S}(0)}. \quad (86)$$

This is the well-known Einstein's formula⁽²⁰⁾ for the generic fluctuations of a parameter κ . From this expression it is possible to calculate the fluctuations of any intensive y_i or extensive X_i thermodynamic variable under generic conditions, as will be shown in the rest of this section.

In order to proceed further we consider an isolated thermodynamic system t with \mathcal{N} degrees of freedom, with entropy $\mathcal{S}^t(X_1^t, X_2^t, \dots, X_{\mathcal{N}}^t)$. The virtual displacement can be imagined as the displacement of an internal closed wall defining an small (but still macroscopic) subsystem. This internal wall prevents the mutual equilibrium (mechanical and/or chemical and/or thermal) between the subsystem and the rest of the system. The displacement produces a change in the extensive variables of the subsystem ΔX_k and of the rest of the system ΔX_k^r , which we assume to behave as a reservoir. Since the global extensive variables do not change:

$$\Delta X_k = -\Delta X_k^r, \quad \forall k = 1, \dots, \mathcal{N}. \quad (87)$$

The total entropy change associated with the virtual displacement is:

$$\Delta \mathcal{S}^t = \Delta \mathcal{S} + \Delta \mathcal{S}^r. \quad (88)$$

For the reservoir we can write:

$$\Delta \mathcal{S}^r = \sum_{k=1}^{\mathcal{N}} y_k^r \Delta X_k^r = -\sum_{k=1}^{\mathcal{N}} y_k^r \Delta X_k, \quad (89)$$

where y_k^r are the conjugated intensive variables of the X_k^r , which remain constant in the reservoir. Let us now describe the subsystem by choosing a set of independent variables $X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}$ which are the natural variables of the Massieu–Planck function $\psi(X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}})$, defined as:

$$\psi = \mathcal{S} - \sum_{k=n+1}^{\mathcal{N}} y_k X_k. \quad (90)$$

Using this equation to calculate $\Delta\mathcal{S}$, substituting into (88) and taking into account (89), we obtain:

$$\Delta\mathcal{S}^t = \Delta\psi + \Delta \left(\sum_{k=n+1}^{\mathcal{N}} y_k X_k \right) - \sum_{k=1}^{\mathcal{N}} y_k^t X_k. \quad (91)$$

By developing this expression, $\Delta\mathcal{S}^t$ can be written as:

$$\Delta\mathcal{S}^t = \Delta\psi - \sum_{k=1}^n y_k^t \Delta X_k + \sum_{k=n+1}^{\mathcal{N}} \langle X_k \rangle \Delta y_k + \sum_{k=n+1}^{\mathcal{N}} \Delta X_k \Delta y_k, \quad (92)$$

where $\langle X_k \rangle$ are the equilibrium values of X_k for the subsystem and reservoir in mutual equilibrium, before the virtual displacement. We expand $\Delta\mathcal{S}^t$ around the initial equilibrium state in terms of the independent variables $X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}$. This yields,

$$\Delta\psi = \sum_{k=1}^n \left(\frac{\partial\psi}{\partial X_k} \right)_0 \Delta X_k + \sum_{k=n+1}^{\mathcal{N}} \left(\frac{\partial\psi}{\partial y_k} \right)_0 \Delta y_k + \frac{1}{2} \vec{\Delta}^T \hat{J} \vec{\Delta} + \mathcal{O}(\Delta^3) \quad (93)$$

where $\vec{\Delta} = (\Delta X_1, \dots, \Delta X_n, \Delta y_{n+1}, \dots, \Delta y_{\mathcal{N}})$ and \hat{J} is the ψ second derivative matrix:

$$\hat{J} = \begin{pmatrix} \left(\frac{\partial^2\psi}{\partial X_1 \partial X_1} \right)_0 & \cdots & \left(\frac{\partial^2\psi}{\partial X_1 \partial y_{\mathcal{N}}} \right)_0 \\ \vdots & & \vdots \\ \left(\frac{\partial^2\psi}{\partial y_{\mathcal{N}} \partial X_1} \right)_0 & \cdots & \left(\frac{\partial^2\psi}{\partial y_{\mathcal{N}} \partial y_{\mathcal{N}}} \right)_0 \end{pmatrix}. \quad (94)$$

where derivatives are evaluated in the state of mutual equilibrium between the reservoir and the subsystem. This is indicated by the subindex 0. We must also expand ΔX_k for $n+1 < k < \mathcal{N}$ up to the same order:

$$\begin{aligned} \Delta X_k &= \sum_{j=1}^n \left(\frac{\partial X_k}{\partial X_j} \right)_0 \Delta X_j + \sum_{j=n+1}^{\mathcal{N}} \left(\frac{\partial X_k}{\partial y_j} \right)_0 \Delta y_j \\ &= - \sum_{j=1}^n \left(\frac{\partial^2\psi}{\partial y_k \partial X_j} \right)_0 \Delta X_j - \sum_{j=n+1}^{\mathcal{N}} \left(\frac{\partial^2\psi}{\partial y_k \partial y_j} \right)_0 \Delta y_j. \end{aligned} \quad (95)$$

Introducing these expansions into Eq. (92) and taking into account the fact that

$$\left(\frac{\partial\psi}{\partial X_k}\right)_0 = y_k^r, \quad \forall k = 1, \dots, n \quad (96)$$

and that

$$\left(\frac{\partial\psi}{\partial y_k}\right)_0 = -\langle X_k \rangle, \quad \forall k = n+1, \dots, \mathcal{N}, \quad (97)$$

we can express $\Delta\mathcal{S}^t$, up to second order in $\vec{\mathcal{A}}$'s (adequate for small fluctuations around equilibrium), as a quadratic form:

$$\Delta\mathcal{S}^t = -\frac{1}{2} \vec{\mathcal{A}}^T \hat{G} \vec{\mathcal{A}} \quad (98)$$

where the matrix \hat{G} is:

$$\hat{G} = \begin{pmatrix} -\left(\frac{\partial^2\psi}{\partial X_1 \partial X_1}\right)_0 & \dots & -\left(\frac{\partial^2\psi}{\partial X_1 \partial X_n}\right)_0 & 0 & \dots & 0 \\ \vdots & & \vdots & \vdots & & \vdots \\ -\left(\frac{\partial^2\psi}{\partial X_n \partial X_1}\right)_0 & \dots & -\left(\frac{\partial^2\psi}{\partial X_n \partial X_n}\right)_0 & 0 & \dots & 0 \\ 0 & \dots & 0 & \left(\frac{\partial^2\psi}{\partial y_{n+1} \partial y_{n+1}}\right)_0 & & 0 \\ \vdots & & \vdots & & \ddots & \\ 0 & \dots & 0 & 0 & & \left(\frac{\partial^2\psi}{\partial y_{\mathcal{N}} \partial y_{\mathcal{N}}}\right)_0 \end{pmatrix}. \quad (99)$$

Therefore, the fluctuations of any set of independent variables are, up to second order, multigaussian:

$$p(\vec{\mathcal{A}}) \propto e^{-\frac{1}{2} \vec{\mathcal{A}}^T \hat{G} \vec{\mathcal{A}}}. \quad (100)$$

The covariance matrix of the fluctuations of the independent variables is the inverse of the matrix \hat{G} . For any generic choice of independent variables, only correlations between extensive variables are expected to

occur. The evaluation of its variances and covariances requires the inversion of the corresponding submatrix. Since this submatrix is diagonal for the intensive variables, we can straightforwardly write:

$$\langle \Delta y_k \Delta y_l \rangle = \delta_{kl} \left(\frac{\partial^2 \psi}{\partial y_k^2} \right)_0^{-1} = \delta_{kl} \left(\frac{\partial y_k}{\partial X_k} \right)_0, \quad (n+1 < k, l < \mathcal{N}), \quad (101)$$

where δ_{kl} is the Kronecker δ -function. Correlations between independent extensive variables $\langle \Delta X_k \Delta X_l \rangle$ ($1 < k, l < n$) are, in general, different to zero.

5. FLUCTUATIONS IN THE STATISTICAL ENSEMBLES

To be more specific, let us apply the generic result obtained in the previous section to the study of fluctuations in the different statistical ensembles. Such statistical fluctuations are restricted by different constraints, as explained in Section 3. Therefore, in each case, and adequate choice of the set of independent variables will simplify the derivation. Let us again, for the sake of clarity, choose the example of a simple pure substance under hydrostatic conditions.

5.1. Microcanonical Ensemble

In this case E , V , and N are fixed. Therefore, we shall evaluate the fluctuations of (i) β at constant V and N , (ii) π at constant E and N and (iii) ν at constant E and V .

(i) in order to evaluate the microcanonical fluctuations of β , we must keep V and N constant. Therefore, the appropriate choice of independent variables is β , V , and N . The corresponding Massieu–Planck potential is Φ [see Eq. (9)]. Therefore we obtain:

$$\langle \Delta \beta^2 \rangle_{V,N} = \left(\frac{\partial^2 \Phi}{\partial \beta^2} \right)_{V,N}^{-1} = - \left(\frac{\partial U}{\partial \beta} \right)_{V,N}^{-1} \quad (102)$$

where the subindices explicitly indicate that the fluctuations correspond to the case of having fixed V and N .

(ii) In this case we choose E , π , and N as independent variables. The adequate Massieu–Planck potential is \mathcal{A} . Therefore:

$$\langle \Delta \pi^2 \rangle_{E,N} = \left(\frac{\partial^2 \mathcal{A}}{\partial \pi^2} \right)_{E,N}^{-1} = - \left(\frac{\partial V}{\partial \pi} \right)_{E,N}^{-1}. \quad (103)$$

(iii) Following the same strategy we obtain:

$$\langle \Delta v^2 \rangle_{E,V} = \left(\frac{\partial^2 \Gamma}{\partial v^2} \right)_{E,V}^{-1} = - \left(\frac{\partial N}{\partial v} \right)_{E,V}^{-1}. \quad (104)$$

Notice that in this ensemble the only fluctuating variables are the intensive variables and, according to the general result of the previous section, there will be no correlations between these variables.

5.2. Canonical Ensemble

In the Canonical ensemble β , V , and N are fixed. The fluctuating variables are E , π , and v . Since only E is an extensive variable, its fluctuations will be uncorrelated with those of π and v . We are therefore, only interested in the evaluation of the fluctuations of (i) E at constant V and N , (ii) π at constant β and N , and (iii) v at constant β and V . The results are:

$$\langle \Delta E^2 \rangle_{V,N} = - \left(\frac{\partial^2 \mathcal{G}}{\partial E^2} \right)_{V,N}^{-1} = - \left(\frac{\partial U}{\partial \beta} \right)_{V,N}, \quad (105)$$

$$\langle \Delta \pi^2 \rangle_{\beta,N} = \left(\frac{\partial^2 \Xi}{\partial \pi^2} \right)_{\beta,N}^{-1} = - \left(\frac{\partial \pi}{\partial V} \right)_{\beta,N}, \quad (106)$$

$$\langle \Delta v^2 \rangle_{\beta,V} = \left(\frac{\partial^2 \Psi}{\partial v^2} \right)_{\beta,V}^{-1} = - \left(\frac{\partial v}{\partial N} \right)_{\beta,V}. \quad (107)$$

It is interesting to note that, from (105) and (102), the microcanonical fluctuations of β and the canonical fluctuations of E (both at constant V and N) are related through the equation:

$$\langle \Delta \beta^2 \rangle_{V,N} \langle \Delta E^2 \rangle_{V,N} = 1. \quad (108)$$

5.3. Grand Canonical Ensemble

For the Grand Canonical ensemble β , V , and v are fixed. Since, in this case, we have two fixed intensive variables, correlations between the two conjugated extensive variables will occur. Therefore, besides the evaluation of the fluctuations of (i) E at constant V and v , (ii) π at constant β and v , and (iii) N at constant β and V , (iv) the correlations $\langle \Delta E \Delta N \rangle_V$ must also be evaluated.

For the evaluation of the first three fluctuations we obtain:

$$\langle \Delta E^2 \rangle_{V,v} = \left(\frac{\partial^2 \Gamma}{\partial E^2} \right)_{V,v}^{-1} = - \left(\frac{\partial E}{\partial \beta} \right)_{V,v}, \quad (109)$$

$$\langle \Delta \pi^2 \rangle_{\beta,v} = \left(\frac{\partial^2 \Pi}{\partial \pi^2} \right)_{\beta,v}^{-1} = - \left(\frac{\partial \pi}{\partial V} \right)_{\beta,v}, \quad (110)$$

$$\langle \Delta N^2 \rangle_{\beta,v} = \left(\frac{\partial^2 \Phi}{\partial N^2} \right)_{\beta,v}^{-1} = - \left(\frac{\partial N}{\partial v} \right)_{\beta,v}. \quad (111)$$

For the evaluation of the correlations between N and E we choose E , V , and N as independent variables. The corresponding potential is \mathcal{S} . In general, the off-diagonal terms in \hat{G} , are different from zero. However, since we are interested in the fluctuations with constant volume ($\Delta V = 0$), the variances and covariances of ΔE and ΔN will be given by the inverse of the sub-matrix \hat{G}_{EN} :

$$\hat{G}_{EN} = \begin{pmatrix} - \left(\frac{\partial^2 \mathcal{S}}{\partial E^2} \right)_{VN} & - \left(\frac{\partial^2 \mathcal{S}}{\partial E \partial N} \right)_V \\ - \left(\frac{\partial^2 \mathcal{S}}{\partial E \partial N} \right)_V & - \left(\frac{\partial^2 \mathcal{S}}{\partial N^2} \right)_{VE} \end{pmatrix} = \begin{pmatrix} - \left(\frac{\partial \beta}{\partial E} \right)_{VN} & - \left(\frac{\partial \beta}{\partial N} \right)_{VE} \\ - \left(\frac{\partial v}{\partial E} \right)_{VN} & - \left(\frac{\partial v}{\partial N} \right)_{VE} \end{pmatrix}. \quad (112)$$

The inverse matrix can be obtained after some algebra, using equations similar to (59). The result is:

$$\hat{G}_{EN}^{-1} = \begin{pmatrix} - \left(\frac{\partial E}{\partial \beta} \right)_{Vv} & - \left(\frac{\partial E}{\partial v} \right)_{\beta V} \\ - \left(\frac{\partial N}{\partial \beta} \right)_{Vv} & - \left(\frac{\partial N}{\partial v} \right)_{V\beta} \end{pmatrix}. \quad (113)$$

The variances (diagonal terms) are exactly the same as those found above in Eqs. (109) and (111) and in Section 3 in Eqs. (55) and (56). The off-diagonal terms correspond to Eq. (57).

5.4. Other Statistical Ensembles

Let us now consider a generic ensemble with n extensive and $\mathcal{N} - n$ intensive fixed variables. The corresponding Massieu–Planck potential is:

$$\psi(X_1, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}) = \mathcal{G} - \sum_{k=n+1}^{\mathcal{N}} X_k y_k. \quad (114)$$

The fluctuating variables are $(y_1, \dots, y_n, X_{n+1}, \dots, X_{\mathcal{N}})$. First, let us evaluate the fluctuations of the intensive variables $\langle \Delta y_i^2 \rangle$ ($i \leq n$). By taking the Massieu–Planck function:

$$\psi'(X_1, \dots, y_i, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}) = \psi - y_i X_i, \quad (115)$$

we will immediately obtain:

$$\begin{aligned} \langle \Delta y_i^2 \rangle &= \left(\frac{\partial^2 \psi'}{\partial y_i^2} \right)_{X_1, \dots, X_{i-1}, X_{i+1}, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}}^{-1} \\ &= - \left(\frac{\partial y_i}{\partial X_i} \right)_{X_1, \dots, X_{i-1}, X_{i+1}, \dots, X_n, y_{n+1}, \dots, y_{\mathcal{N}}}. \end{aligned} \quad (116)$$

The correlations between any two intensive variables vanish. In other words, $\langle \Delta y_i \Delta y_j \rangle = 0$ ($i, j \leq n$). To show this it is sufficient to consider the Massieu–Planck function $\psi'' = \psi - y_i X_i - y_j X_j$, and realize that all the off-diagonal terms in the \hat{G} matrix corresponding to intensive variables will be zero. For the computation of the fluctuations of the extensive variables $\langle \Delta X_i^2 \rangle$ ($i > n$), we perform a Legendre inverse transform of ψ into ψ' :

$$\psi' = (X_1, \dots, X_n, y_{n+1}, \dots, X_i, \dots, y_{\mathcal{N}}) = \psi + y_i X_i, \quad (117)$$

and obtain:

$$\begin{aligned} \langle \Delta X_i^2 \rangle &= - \left(\frac{\partial^2 \psi'}{\partial X_i^2} \right)_{X_1, \dots, X_n, y_{n+1}, \dots, y_{i-1}, y_{i+1}, \dots, y_{\mathcal{N}}}^{-1} \\ &= - \left(\frac{\partial X_i}{\partial y_i} \right)_{X_1, \dots, X_n, y_{n+1}, \dots, y_{i-1}, y_{i+1}, \dots, y_{\mathcal{N}}}. \end{aligned} \quad (118)$$

The comparison of this result with Eq. (116) enables us to generalize the Eq. (108) relating the fluctuations of an extensive variable with the fluctuations of the corresponding intensive variable. The general result is:

$$\langle \Delta X_i^2 \rangle \langle \Delta y_i^2 \rangle = 1, \quad (119)$$

where both averages correspond to keeping all the variables except X_i or y_i constant. This expression means that it is not possible to prevent both an extensive variable and the corresponding conjugated intensive variable to fluctuate simultaneously.⁽²¹⁾

We can also evaluate the correlations $\langle \Delta X_i \Delta X_j \rangle$ ($i, j > n$). Taking the Massieu–Planck potential

$$\psi'' = \psi + y_i X_i + y_j X_j \tag{120}$$

one finds:

$$\hat{G}_{X_i X_j}^{-1} = \begin{pmatrix} -\left(\frac{\partial X_i}{\partial y_i}\right)_{\dots y_j \dots} & -\left(\frac{\partial X_i}{\partial y_j}\right)_{\dots y_i \dots} \\ -\left(\frac{\partial X_j}{\partial y_i}\right)_{\dots y_j \dots} & -\left(\frac{\partial X_j}{\partial y_j}\right)_{\dots y_i \dots} \end{pmatrix} \tag{121}$$

which is symmetrical. It is also easy to check that the correlations between extensive and intensive variables are null. By using the method presented so far, for this generalized ensemble, one may also compute correlations of more than two variables: $\langle \Delta X_i \Delta X_j \Delta X_k \rangle$. Relations similar to those given in Eqs. (119) can also be found between such higher order fluctuations.

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