Disequilibrium, thermodynamic relations, and Rényi's entropy

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A B S T R A C T

The disequilibrium concept (D) was introduced by López-Ruiz, Mancini, and Calbet 20 years ago together with their successful notion of statistical complexity. In this note we show that, in a classical, canonical-ensemble environment, D displays interesting thermodynamic properties and is able to replace the partition function. Also, we show that for a generalized Statistical Complexity-family that involves Rényi's entropy of order q, the maximal value of these new complexities is attained in the case $q = 1$.

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1. Introduction

Even if one is cognizant about the degree of unpredictability and randomness of a system this does not at all mean that one can properly grasp the existing correlation-structures, that strongly influence the prevailing probability distribution (PD). Of course, one would want to capture the relationship among a system's components in the way that the entropy captures disorder. The pair of concepts randomness-structural correlations shares common components. It is true that the opposite extremal situations of (i) perfect order and (ii) maximal randomness are not endowed with major structural correlations [1]. In between (i) and (ii) a variegated range of structure-degrees can exist. These, naturally, would be reflected by the features of the above mentioned PD. In which way? The answer is rather complex. Crutchfield noted in 1994 that "Physics does have the tools for detecting and measuring complete order equilibria and fixed point or periodic behavior and ideal randomness via temperature and thermodynamic entropy or, in dynamical contexts, via the Shannon entropy rate and Kolmogorov complexity. What is still needed, though, is a definition of structure and a way to detect and to measure it" [2,3]. Notoriously, Seth Lloyd enumerated as many as 40 ways of defining complexity, none of them satisfactory enough.

As stated above, we wish that some adequate functional of the probability distribution may enable one to grasp correlations

as entropy captures randomness. A really great breakthrough was reached by the complexity-definition of López-Ruiz, Mancini and Calbet (LMC) [1]. LMC's complexity did separate and quantify contributions coming from Shannon's entropy or information H and structure. The structural part was assigned to the concept of disequilibrium, denoted by D, that measures in probability space the distance from the actual PD to the uniform one, whose form for an N-particle system is given by

$$D = \sum_{i=1}^{N} \left(p_i - \frac{1}{N} \right)^2, \tag{1}$$

where $p_1, p_2, \ldots, p_N$ are the corresponding probabilities, with the condition $\sum_{i=1}^{N} p_i = 1$ [1].

LMC's complexity definition reads $C_{LMC} = DH$, and is also called the statistical complexity (see, for instance, Refs. [1,4–9]). C_{LMC} vanishes, at it should, in the two special extreme instances (i) and (ii) cited above. Additionally, we mention in passing a slightly modified complexity (C) definition introduced by Catalan et al. in Ref. [13], to avoid possible negative C-values. This new C is of the form

$$C = D e^{H}. \tag{2}$$

In this effort we will focus attention, within a canonical-ensemble environment, on the LMC disequilibrium concept and show that for classical integrable systems there is a consistent thermodynamic description related to it. Indeed, D entirely replaces the partition functions in the ensuing relationships. We emphasize the fact that D is a distance in probability space, and that

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such a distance is endowed with interesting thermodynamic properties. Our motivation is to reinforce the idea that the LMC-one is a correct version of statistical complexity, although not the only one, of course. Given the great number of alternative proposals, we are able to show that the LMC-one is at least maximal within the family of Rényi-related complexities.

The paper is organized as follows. Section 2 introduces some preliminary materials. Our results are presented in the Sections 3 and 4 and some conclusions are drawn in Section 5.

2. LMC disequilibrium in the canonical ensemble

We devote this preparatory section to present important ideas proposed by López-Ruiz for the canonical ensemble in Ref. [10]. In this reference an ideal gas in thermal equilibrium is discussed. Let us deal then with a classical system of N identical particles, confined into a space of volume V, in thermal equilibrium at temperature T. The corresponding Boltzmann distribution becomes [11]

$$\rho(x, p) = \frac{e^{-\beta \mathcal{H}(x,p)}}{Q_N(V, T)}, \tag{3}$$

with $\beta = 1/k_B T$, k_B the Boltzmann constant, $\mathcal{H}(x, p)$ the Hamiltonian, and x, p the concomitant phase space variables. The canonical partition function is

$$Q_N(V, T) = \int d\Omega \, e^{-\beta \mathcal{H}(x,p)}, \tag{4}$$

with $d\Omega = d^{3N}x \, d^{3N}p / N! h^{3N}$. It is well known that the Helmholtz' free energy A is written as [11]

$$A(N, V, T) = -k_B T \ln Q_N(V, T). \tag{5}$$

R. López-Ruiz shows in Ref. [10] that the canonical disequilibrium $D(N, V, T)$ adopts the following quite interesting aspect

$$D(N, V, T) = e^{2\beta [A(N,V,T) - A(N,V,T/2)]}. \tag{6}$$

Notice that this form is valid only for continuous probability distributions. So as better grasp the meaning of Eq. (6), changing now T by $T/2$ in Eq. (5) and replacing this into Eq. (6), one finally encounters that

$$D(N, V, T) = \frac{Q_N(V, T/2)}{[Q_N(V, T)]^2}. \tag{7}$$

A better known, alternative D-expression can be gotten. Employing now definitions (3) and (4), D can also be cast as

$$D(N, V, T) = \frac{\int d\Omega \, e^{-2\beta \mathcal{H}(x,p)}}{[Q_N(V, T)]^2} = \int d\Omega \, [\rho(x, p)]^2. \tag{8}$$

This is the orthodox form used by most people (see, for instance, Ref. [12]).

3. Disequilibrium and thermodynamic relations

We assume now that the canonical, classical disequilibrium $D(N, V, T)$, given by (8), is known. Next, we proceed to investigate D-connections with some thermodynamic relations to gain insight into its thermodynamic role.

For pedagogical reasons, we list here the most important thermodynamic relations (we will call them, with a touch of subjectivity, the relevant ones) in the canonical ensemble. Assuming we know the free energy (5), the rest of the relevant relations are

$$U = -\left(\frac{\partial \ln Q_N(V, T)}{\partial \beta} \right)_{N,V}, \tag{9}$$

$$\mu = -k_B T \left(\frac{\partial \ln Q_N(V, T)}{\partial N} \right)_{V,T}, \tag{10}$$

$$p = k_B T \left(\frac{\partial \ln Q_N(V, T)}{\partial V} \right)_{N,T}, \tag{11}$$

$$S = k_B \left(\frac{\partial (T \ln Q_N(V, T))}{\partial T} \right)_{N,V}, \tag{12}$$

for the mean energy, chemical potential, pressure, and entropy, respectively. All these quantities depend on the variables N, V and T. However, in order to gain some space with the notation, we retain this dependence only for the disequilibrium, Statistical Complexity, and free energy. In the remaining thermodynamic quantities, we will add the variables only when strictly necessary.

The idea now is recast these thermal relations in a disequilibrium parlance. This is done as follows.

3.1. Connection with the mean energy

Taking the derivative respect to β in Eq. (7), it is easy to arrive at

$$\left(\frac{\partial \ln D(N, V, T)}{\partial \beta} \right)_{N,V} = \left(\frac{\partial \ln Q_N(V, T/2)}{\partial \beta} \right)_{N,V} - 2 \left(\frac{\partial \ln Q_N(V, T)}{\partial \beta} \right)_{N,V}. \tag{13}$$

Appealing to the definition of mean value of energy (9) and replacing it into Eq. (13), we immediately get a first relation between the disequilibrium and the mean energy

$$\left(\frac{\partial \ln D(N, V, T)}{\partial \beta} \right)_{N,V} = 2(U(T) - U(T/2)). \tag{14}$$

The classical Equipartition Theorem of energy, valid in the case of quadratic dependence of energy on the variable under consideration [14,15], asserts that

$$U = \frac{f}{2} k_B T, \tag{15}$$

where f is the number of the system's degrees of freedom. Note that we have dropped the dependence on V and N. Accordingly, from Eq. (15), we obviously have $U(T/2) = U(T)/2$. Therefore, introducing this and Eqs. (15) into Eq. (14) we obtain

$$\left(\frac{\partial \ln D(N, V, T)}{\partial \beta} \right)_{N,V} = U. \tag{16}$$

Notice that the relation (14) is more general than (16), since this last identity holds for systems that satisfy equipartition of energy.

Moreover, differentiating Eq. (7) respect to the mean energy U we get

$$\left(\frac{\partial \ln D(N, V, T)}{\partial U} \right)_{N,V} = \left(\frac{\partial \ln Q_N(V, T/2)}{\partial U} \right)_{N,V} - 2 \left(\frac{\partial \ln Q_N(V, T)}{\partial U} \right)_{N,V}. \tag{17}$$

Since U is related to β through Eq. (15), we also have that $\beta = (\partial \ln Q_N / \partial U)_{N,V}$. Thus, assuming again equipartition of energy, we immediately find

$$\left(\frac{\partial \ln D(N, V, T)}{\partial U} \right)_{N,V} = -\beta. \tag{18}$$

Therefore, the couple of Eqs. (16) and (18) would constitute the basic set of equations, called reciprocity relations, of a thermal Information Theory à la Jaynes, that would yield a complete description of the thermodynamic properties of the system in D-language [16]. This is a nice result!

3.2. Connection with the thermodynamic entropy

We begin taking the derivative of Eq. (6) with respect the temperature T, for V and N fixed. One has

$$\left[\frac{\partial}{\partial T}\left(k_B T \ln D(N, V, T)\right)\right]_{N,V}$$
$$= 2\left[\left(\frac{\partial A(N, V, T)}{\partial T}\right)_{N,V} - \left(\frac{\partial A(N, V, T/2)}{\partial T}\right)_{N,V}\right]. \quad (19)$$

By using the well-known thermodynamic relation for the entropy (12) and the free energy (5) one reaches

$$\left[\frac{\partial}{\partial T}\left(k_B T \ln D(N, V, T)\right)\right]_{N,V} = S(T/2) - 2S(T). \quad (20)$$

3.3. Connection with the pressure

We connect the pressure with the disequilibrium through Eq. (7) and invoking the thermodynamic relation (11). Then, we arrive at

$$\left(\frac{\partial \ln D(N, V, T)}{\partial V}\right)_{N,T} = \frac{2}{k_B T}\left(p(T) - p(T/2)\right). \quad (21)$$

3.4. Connection with the chemical potential

Starting from the disequilibrium-concept (6) and differentiating with respect to N (V and T fixed), and invoking the thermodynamic relation for the chemical potential in the canonical ensemble, i.e., Eq. (10), we are led to

$$\left(\frac{\partial \ln D(N, V, T)}{\partial N}\right)_{V,T} = \frac{2}{k_B T}\left(\mu(T) - \mu(T/2)\right). \quad (22)$$

3.5. Connection with the specific heat and fluctuations of energy

Consider the specific heat at constant volume V. It is defined as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -\frac{1}{k_B T^2}\left(\frac{\partial U}{\partial \beta}\right)_{N,V}. \quad (23)$$

Using Eq. (14) we find

$$C_V = -\frac{2}{k_B T^2}\left[\left(\frac{\partial U(T)}{\partial \beta}\right)_{N,V} - \left(\frac{\partial U(T/2)}{\partial \beta}\right)_{N,V}\right]. \quad (24)$$

Using the definition (16) we are led to an alternative definition of C_V in terms of the disequilibrium, whose form is

$$C_V = -\frac{1}{k_B T^2}\left(\frac{\partial^2 \ln D(N, V, T)}{\partial \beta^2}\right)_{N,V}. \quad (25)$$

It is known that the energy-fluctuations in the canonical ensemble lead to $(\Delta U)^2 \equiv \langle \mathcal{H}^2\rangle - \langle \mathcal{H}\rangle^2 = k_B T^2 C_V$, so that, utilizing Eq. (25), we obtain the follows relationships

$$(\Delta U)^2 = -\left(\frac{\partial^2 \ln D(N, V, T)}{\partial \beta^2}\right)_{N,V}. \quad (26)$$

3.6. Connection with Statistical Complexity

We begin considering the general definition of Statistical Complexity given by Eq. (2) with H any entropic functional (as explained in the Introduction). Taking the logarithm of C one finds

$$H = \ln\left(C D^{-1}\right). \quad (27)$$

Now, taking derivatives with respect to the mean energy U (with N and V fixed), we get

$$\left(\frac{\partial H}{\partial U}\right)_{N,V} = \left(\frac{\partial \ln C}{\partial U}\right)_{N,V} - \left(\frac{\partial \ln D}{\partial U}\right)_{N,V}. \quad (28)$$

Invoking the Eq. (18), we find

$$\left(\frac{\partial \ln C}{\partial U}\right)_{N,V} = -\beta + \left(\frac{\partial H}{\partial U}\right)_{N,V}, \quad (29)$$

which constitutes the necessary condition for C in order to have a D compatible with Thermodynamics as described by the canonical ensemble.

As a particular case, we rename in Eq. (29) the entropy $H = S/k_B$, with S the thermodynamic entropy and invoking the known relation for the thermodynamic temperature $(\partial S/\partial U)_{N,V} = 1/T$, we find

$$\left(\frac{\partial \ln C}{\partial U}\right)_{N,V} = 0. \quad (30)$$

On could in this way conclude then that the definition of Statistical Complexity given by Eq. (2) is compatible with canonical-ensemble thermodynamics provided that it compliance Eq. (30).

4. Connection with Rényi's entropy

Other entropic functional of great relevance is the Rényi's entropy, because of its connection with the free energy, as explained in Ref. [17].

The Rényi's entropy of order q for a classical system is defined as

$$R_q = \frac{k_B}{1-q}\ln\int d\Omega\,[\rho(x, p)]^q, \quad (31)$$

where $0 < q < \infty$. For $q = 1$ we get the usual thermodynamic entropy $R_1 \equiv S$. We have added, for convenience, the Boltzmann constant in the definition of R_q.

Baez [17] noted that, while Shannon's entropy has a strong thermodynamic' flavor, the Rényi's entropy S_q has not been completely integrated into this subject. Baez shows that it is not necessary to modify statistical mechanics to find a natural role for Rényi's entropy in physics. This role is related to the free energy, using a parameter $q = T/T_0$ defined as a ratio of temperatures. It was shown by Baez that the relation between Rényi's entropy and the free energy A is given by Eq. (9) of Ref. [17]

$$R_{T_0/T}(N, V, T_0) = -\frac{A(N, V, T) - A(N, V, T/2)}{k_B(T - T_0)}. \quad (32)$$

If we set $T_0 = T/2$ and use Eq. (6), we obtain

$$D(N, V, T) = e^{-R_{1/2}(N, V, T/2)}, \quad (33)$$

which expresses a relation between Rényi's entropy and disequilibrium, such that it is possible to reconstruct the thermodynamic relations utilizing any of these three quantities. In addition, by using Eq. (2), we re-express the Statistical Complexity as

$$C(N, V, T) = e^{S(N, V, T)/k_B - R_{1/2}(N, V, T/2)}, \quad (34)$$

which looks like a sort of distance between Rényi's and Shannon's entropies. Moreover, we can explore other, more general definitions of Statistical Complexity using the Rényi's measure. We propose here to adopts one version of the form

$$C_q(N, V, T) = e^{R_q(N,V,T)/k_B - R_{1/2}(N,V,T/2)}, \tag{35}$$

that, for $q = 1$, coincides with Eq. (34). Applying Eq. (29), with $H = R_q/k_B$, we get

$$\left(\frac{\partial \ln C_q}{\partial U} \right)_{N,V} = -\beta + \frac{1}{k_B} \left(\frac{\partial R_q}{\partial U} \right)_{N,V}. \tag{36}$$

Since, as it was shown in Ref. [18] (and references therein), that $\left(\partial R_q / \partial U \right)_{N,V} = 1/T$, then we obtain

$$\left(\frac{\partial \ln C_q}{\partial U} \right)_{N,V} = 0, \tag{37}$$

which it is true for all q.

4.1. Statistical Complexity bounds

The main property of the Rényi's entropy is that it is concave for $0 < q \leq 1$ and neither concave nor convex for $q > 1$ respect to the probabilities. Because the concavity property is required by the maximum entropy principle [16,19], we restrict our treatment to $0 < q \leq 1$. From Eq. (35) we get

$$R_q - S = k_B \ln \left(C_q/C \right). \tag{38}$$

On the other hand, we observe, for $0 < q \leq 1$, that $\rho^q \geq \rho \ln \rho$. Integrating both members by $\int d\Omega$, and after a bit of algebra, we get

$$S/k_B \geq - \int d\Omega \, [\rho(x, p)]^q, \tag{39}$$

so that, taking into account the definition of Rényi's entropy (31) we find the inequality

$$S/k_B \geq -e^{(1-q)R_q/k_B}. \tag{40}$$

Appealing to Eqs. (38) and (40), we arrive at

$$\ln \left(C_q/C \right) \leq R_q/k_B + e^{(1-q)R_q/k_B}. \tag{41}$$

Since $R_q \geq 0$, this entails

$$\ln \left(C_q/C \right) \leq 1, \tag{42}$$

implying

$$0 \leq C_q \leq C, \tag{43}$$

where we have considered that $C_q/C \geq 0$ for all q because the complexities are positive definite. We conclude that the maximum Statistical Complexity is attained by the LMC C.

5. Conclusions

We have shown in this note that, in a classical phase space context with continuous probability distributions, the LMC notion of disequilibrium D has a suitable role in statistical thermodynamics. Indeed, in our new thermal relations, the partition function Q_N does not appear, so that one may be tempted to suggest that it has been replaced by the disequilibrium. All important thermodynamic relations can indeed be expressed in terms of D. One might argue that the logarithm of D exhibits properties analogous to those of Massieu potentials.

We have also used a generalized LMC-like complexity-family that involves Rényi's entropy instead of Shannon's

$$C_q(N, V, T) = e^{R_q(N,V,T)/k_B - R_{1/2}(N,V,T/2)},$$

and shown that $C_{q=1}$ is maximal for this family.

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