Thermodynamic non-additivity in disordered systems

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It is shown that there is a mapping of the replica approach to disordered systems with finite replica index \( n \) on the Tsallis non-extensive statistics, if the average thermodynamic entropy differs from the information entropy for the probability distribution. In the case of incomplete information the entropic index \( q = 1 - n \) is shown to be related to the degree of lost information.

I. INTRODUCTION

The non-extensive thermodynamics results from a generalization [1] of the standard Gibbs-Boltzmann (GB) statistics. The non-extensive formalism has been applied to the description of a variety of physical systems [2]. In some cases, related to disordered systems (e.g. anomalous diffusion in porous media or surface growth [3,4]), it has resulted in quantitative implications, which are difficult to obtain in the framework of the classical GB approach.

In the spirit of the information theory approach [5] the non-extensivity is usually introduced starting with a postulation of the entropy measure. For instance, Tsallis proposed [1] the following form

\[
S_q^T = \frac{1 - \int (d\sigma)p(\sigma)\beta\varepsilon(\sigma)}{q - 1}
\]

where \( p(\sigma) \) is a probability to find a state \( \sigma \), with \( \int (d\sigma)p(\sigma) = 1 \). Here \( q \) is an index, corresponding to a given statistics. Simultaneously \( q \) is a measure of the thermodynamic non-additivity. Although in general the non-extensivity should be distinguished [6] from the non-additivity, quite often these two terms are being used as synonymous.

If the state \( \sigma \) is characterized by the energy \( \varepsilon(\sigma) \), then, based on the entropy maximization under a constraint for a generalized internal energy, one obtains [7,8] a power law for the probability

\[
p(\sigma) = \frac{[1 - (1 - q)\beta\varepsilon(\sigma)]^{1/(1-q)}}{\int (d\sigma)[1 - (1 - q)\beta\varepsilon(\sigma)]^{1/(1-q)}}
\]

We do not discuss here how the above distribution modifies with different constraints [8] for the internal energy as well as the internal specificities [8] of the Tsallis theory and its mathematical consistency. For any constraint [8] in the limit \( q \to 1 \) one recovers the standard GB results:

\[
S_{GB} = -\frac{\int (d\sigma)p(\sigma)\ln p(\sigma)}{1 - (1 - q)\beta\varepsilon(\sigma)}
\]

Note that the Tsallis form is not unique in having \( S_{GB} \) as a limit. As an alternative example, one can consider the Renyi form [9], which is however additive.

Despite of many efforts [10,11] towards deriving the Tsallis-type entropy starting from basic assumptions, up to now it is not clear which physical systems are "naturally" non-extensive, and thus require the Tsallis-type statistics as an essential tool. In particular, the physical meaning of the \( q \) parameter [12–15] as well as a relation of \( S_q^T \) to an underlying dynamics [16] are still under discussion. Also the thermodynamic consistency of the non-extensive formalism has recently been criticized [17]. Therefore, a derivation of the power-law entropy (like \( S_q^T \)) instead of postulating it, would be much helpful in resolving these problems.

In this paper we investigate the conditions and assumptions at which the non-extensive thermodynamics can be recovered using the tools of the standard statistical mechanics, applied to systems which, because of their complexity, require more than the usual Hamiltonian description. This is in the spirit of the Beck-Cohen approach [18], who have shown that a non-GB distribution (including the Tsallis one) could appear in systems with fluctuating intensive quantities. Our purpose is to recover the Tsallis-type entropy, which is a generating functional for the power-like probability distribution, but not to construct the distribution itself. This establishes a relation between the information theory and the statistical mechanics in application to systems which are out of the conventional GB equilibrium. In particular we focus on disordered systems since their description involves two essential ingredients: a Hamiltonian and a distribution function. In fact, Tsallis has already commented [19] on a formal similarity of the non-extensive formalism and the replica trick, suitable for the systems with a quenched disorder. Therefore it is tempting to realize the condition at which such systems exhibit the non-extensive behavior. This would allow us to make a link between the system dynamics (the Hamiltonian), its complexity (the probability distribution) and the magnitude of the entropic \( q \)-parameter.

II. REPLICA APPROACH TO DISORDERED SYSTEMS

From a dynamical point of view disordered systems (like porous materials [20] or spin glasses [21])
can be viewed as those consisting of many subsystems, whose equilibration times are much different [22]. Then, considering the static (or "equilibrium") properties, the slower subsystem, say \( \{s\} \), is quenched with a given probability distribution \( P(\sigma) \), while the faster one, say \( \{s\} \) is governed by a Hamiltonian \( H = H_R + H[\sigma,s] \). In the case of spin glasses the counterparts of \( \{s\} \) and \( \{\sigma\} \) systems are the spin variables and the random fields (or exchange constants), respectively. It is essential that the Hamiltonian contains a reference part \( H_R \), which gives a characteristic energy scale reflecting the way of quenching (e.g. the cooling rate and the correspondent temperature gap).

For a given configuration \( \{\sigma\} \) one can calculate the partition function

\[
Z(\sigma) = Z/Z_R = \int (ds) e^{-\beta H[\sigma;s]} \tag{3}
\]

where \( Z_R = e^{-\beta H_R} \) and \( \beta = 1/kT \). Then all the thermodynamic characteristics are known. For instance, the free energy excess

\[
F(\sigma) = F - H_R = -\frac{1}{\beta} \ln Z(\sigma) \tag{4}
\]

and the internal energy excess

\[
U(\sigma) = U - H_R = -\frac{d}{d\beta} \ln Z(\sigma) \tag{5}
\]

determine the thermodynamic entropy

\[
S_T(\sigma) = \beta[U(\sigma) - F(\sigma)] \tag{6}
\]

Then all the relevant thermodynamic quantities can be obtained by averaging the quenched ones. For instance, the average free energy is given by

\[
F = \overline{F}(\sigma) = \int (d\sigma) P(\sigma) F(\sigma) \tag{7}
\]

Note that, in contrast to the conventional equilibrium, now we have two entropies - the thermodynamic entropy

\[
S_T = \int (d\sigma) P(\sigma) S_T(\sigma) \tag{8}
\]

and the one related to the information on the probability distribution

\[
S_I = -\int (d\sigma) P(\sigma) \ln P(\sigma) \tag{9}
\]

Instead of the direct averaging of the logarithm in (7) it is convenient to introduce the replica trick \([23]\), which is based on the representation

\[
\ln Z(\sigma) = \lim_{n \to 0} \frac{[Z(\sigma)]^n - 1}{n} \tag{10}
\]

It is equivalent to making \( n \) noninteracting copies of the system. Nevertheless the copies are not completely independent because the probability distribution \( P(\sigma) \) is the same for all of them. Then the problem reduces to the evaluation of the moments \( [Z(\sigma)]^n \), which is expected to be a simpler task \([24]\). Note, however, that such a procedure is not just a trick. In fact, the behavior of one system (e.g. a spin glass) is interpreted as a limiting case of another system (the one with \( n \neq 0 \)). Such that the quenched average is expressed through a "weighted" annealed average for a more complex system, involving an extension of the phase space \([25]\). The systems with \( n \neq 0 \) were considered \([26–28]\) in application to the spin glasses and neural networks \([29]\). In the context of spin models such a system can be viewed as a collection of \( n \) domains of interacting spins with a common probability distribution \( P(\sigma) \). Note, however that due to the limiting procedure in eq. (10) the replica index \( n \) can be non-integer \([24]\)- i.e. at least for \( 0 \leq n \leq 1 \) it must vary continuously. Sherrington \([26]\) has investigated the critical behavior of such replica magnets, driven by the inter- and intra-replica interaction. Moreover, Derrida has shown \([30]\), that there is a mapping between the random walk, the random energy model and the replica results for non-zero \( n \).

Based on the discussion above we allow \( n \) to be finite. The \( \sigma \)-dependent functions, like \( F(\sigma) \), obey the standard statistical thermodynamics, since \( \sigma \) is a parameter (although known only statistically at the level of \( F(\sigma) \) evaluation). The average free energy is now \( n \)-dependent

\[
F_n = \overline{F}_n(\sigma) = -\frac{1}{\beta} \int (d\sigma) P(\sigma) \frac{[Z(\sigma)]^n - 1}{n} \tag{11}
\]

The internal energy \( U_n \) can be found as a counterpart of the internal energy (5) and the average internal energy

\[
U_n = -\frac{1}{\beta} \int (d\sigma) P(\sigma) [Z(\sigma)]^{n-1} dZ(\sigma)/d\beta \tag{12}
\]

can be rearranged to the form

\[
U_n = \int (d\sigma) P(\sigma) [Z(\sigma)]^n U(\sigma) \tag{13}
\]

If \( \sigma \)-dependent quantities obey the standard thermodynamic relation \( F(\sigma) = U(\sigma) - S_T(\sigma)/\beta \), then the counterpart of the entropy is given by

\[
S_n = \int (d\sigma) P(\sigma) \left[ \frac{[Z(\sigma)]^n (1 + n\beta U(\sigma) - 1)}{n} \right] \tag{14}
\]
III. MAPPING ON THE TSALLIS THEORY

Starting from eq. (14) and replacing $n$ by $1-q$ we can rearrange the correspondent thermodynamic entropy $S_q$ to the Tsallis construction

$$S_q = \frac{1 - \int (d\sigma) \Pi(\sigma)^q}{q - 1} \tag{15}$$

where $\Pi(\sigma)$ is given by

$$\Pi(\sigma) = [P(\sigma)[Z(\sigma)]^{1-q}(1 + (1-q)\beta U(\sigma))]^{1/q} \tag{16}$$

At this level our calculations are purely formal, and $S_q$ is equivalent to $S_n$. In order to obtain $S_q$ coherently with the Tsallis conjecture we have to associate $\Pi(\sigma)$ with a probability distribution. Then we naturally impose two restrictions:

$$\Pi(\sigma) \geq 0; \quad \int (d\sigma) \Pi(\sigma) = 1 \tag{17}$$

From the positivity condition we have

$$q \leq 1 + \frac{1}{\beta U(\sigma)} \tag{18}$$

which is equivalent to the cut-off condition [8] in the Tsallis approach.

In order to realize the meaning of $q \neq 1$ we expand $\Pi(\sigma)$, given by eq. (16), around $q = 1$ up to the second order

$$\Pi(\sigma) = P(\sigma) - P(\sigma)D(\sigma)(q - 1) + P(\sigma) \left[ D(\sigma) + \frac{1}{2} (D^2(\sigma) - \beta^2 U^2(\sigma)) \right] (q - 1)^2 \tag{19}$$

where $D(\sigma) = S_T(\sigma) + \ln P(\sigma)$. Therefore, we see that the probability distribution differs from $P(\sigma)$ as long as $q \neq 1$. Moreover, the magnitude of $q$ is coupled to the $\sigma$-dependent thermodynamics and to a shape of $P(\sigma)$.

From the normalization condition we obtain

$$-\Delta S(q - 1) + [\Delta S + \Sigma](q - 1)^2 = 0 \tag{20}$$

where

$$\Delta S = \int (d\sigma) P(\sigma)D(\sigma) = S_T - S_I \tag{21}$$

is the difference of the thermodynamic and the information entropies and $\Sigma$ is given by

$$\Sigma = \frac{1}{2} \int (d\sigma) P(\sigma) \left[ D^2(\sigma) - \beta^2 U^2(\sigma) \right] \tag{22}$$

Then solving eq. (20) with respect to $q$ we obtain the result

$$q - 1 = \frac{\Delta S}{\Delta S + \Sigma} \tag{23}$$

suggesting that small deviations of $q$ from 1 are determined by the difference $\Delta S$ of the thermodynamic and the information entropies. Comparing eqs. (8) and (9) we can easily demonstrate that these two entropic impacts are equal only if the probability distribution is consistent with the thermodynamic fluctuations [31]: $P(\sigma) \propto \exp(-\beta S_T(\sigma))$. Therefore, $\Delta S$ (and consequently $q$) can be viewed as a measure of the deviation from the conventional thermodynamic equilibrium. Similar conjectures were drawn in ref. [32], discussing the fluctuations within the Tsallis statistics. Since the sign of $\Delta S$ and $\Sigma$ is not fixed, then from eq. (23) we can have both $q > 1$ and $q < 1$. Nevertheless, $q$ is related to the replica index $n$ through $n = 1 - q$. Therefore, if $n \geq 0$ (as it is usually assumed in the spin glass theories), then we deal with $q \leq 1$.

On the other hand $\Delta S$ depends explicitly on the thermodynamic parameters and on a shape of the quenching distribution. Therefore, there is a mapping of the replica approach with a non-zero replica index $n = 1-q$ onto the Tsallis theory, provided that the replica index varies coherently with the system thermodynamics and the probability distribution. This conclusion agrees with the results obtained within the incomplete information theory [33] which suggests that the $q$ parameter is related to the thermodynamic quantities. In the case when the thermodynamic parameters are fixed, the magnitude of $q$ is related to the parameters of the probability distribution. If, for instance, $P(\sigma)$ is of the gaussian form, then the width of this distribution determines the fluctuation $\sigma^2 - \bar{\sigma}^2$. In other words the magnitude of $q$ is related to the fluctuation of the parameters in the quenching distribution. In some sense, this result is coherent with the one [14] obtained for the generalized exponential distribution.

IV. INCOMPLETE INFORMATION

As is discussed above, due to fact that $q \neq 1$, we deal with the weighted annealed averaging (see eq. (14)). That is, in contrast to the usual quenching ($q = 1$) we have a nonvanishing feed-back effect on $\{\sigma\}$-distribution from the thermodynamics of $\{s\}$-subsystem (see eq. (19)). As a result we operate with the probability distribution $\Pi(\sigma)$, involving the thermodynamic quantities, instead of $P(\sigma)$ which corresponds to the case when $\{\sigma\}$-subsystem remains unchanged. This situation is similar to what is reported [28,29] for partially annealed systems.

Taking the porous materials [20] as an example, we can associate $P(\sigma)$ with the empty matrix (e.g.
pore size distribution) and $\Pi(\sigma)$ - with the matrix in the presence of an adsorbed fluid. In general, the latter changes the matrix properties. For instance, by the analogy with the intercalation system [34,35], we can expect a change of the matrix volume upon the fluid absorption. Moreover, quite often the adsorbates induce a new ordering [36] of the substrates or facilitate their disordering [37] depending upon the specificities of the adsorbate-substrate interaction. Therefore, because of a complicated fluid-matrix coupling, our information on the pore size distribution could be incomplete [33]

$$\int (d\sigma)P(\sigma) = 1; \quad \int (d\sigma)\Pi(\sigma) = \Lambda \neq 1 \quad (24)$$

where $1 - \Lambda$ can be considered as a degree of lost information. In this case we can rearrange (14) to the following form

$$S_q = -\int (d\sigma)\Pi(\sigma) \frac{[\Pi(\sigma)]^q - 1}{q - 1} \quad (25)$$

where $\Pi(\sigma)$ should be found from (if $q \neq 1$)

$$[\Pi(\sigma)]^q - \Pi(\sigma) = P(\sigma) \left[ (Z(\sigma))^{1-q} \{ 1 + (1-q)\beta U(\sigma) \} - 1 \right] \quad (26)$$

For small $1 - \Lambda$ the distribution $\Pi(\sigma)$ should exhibit small deviations from that given by eq. (16). Therefore, we determine $\Pi(\sigma)$ perturbatively, taking eq. (16) as a zeroth approximation. Then, expanding around $q = 1$, we find that the linear approximation is the same as that in eq. (19)

$$\Pi(\sigma) = P(\sigma) - P(\sigma)D(\sigma)(q - 1) \quad (27)$$

From the incomplete normalization condition (24) we obtain

$$q = 1 + \frac{1 - \Lambda}{\Delta S} \quad (28)$$

which demonstrates that the entropic index $q$ is related to the degree of lost information ($1 - \Lambda$). In the limit $\Lambda \to 1$ we must retain the quadratic term in (27) and then we recover our previous result (23).

V. CONCLUSION

A relation between the non-extensive Tsallis statistics and the replica formalism for disordered systems is discussed. The key specificity of this kind of systems is the splitting into subsystems with different levels of description, i.e. the Hamiltonian and the probability distribution. Due to this one necessarily operates with two entropic impacts: the thermodynamic and the information entropies. It is shown that there is a mapping of

the replica approach to disordered systems on the Tsallis theory with $q \neq 1$, if the average thermodynamic entropy differs from the information entropy related to the probability distribution. In the case of incomplete information the entropic index deviates from unity proportionally to the degree of lost information. Therefore, the magnitude of $q$ depends on the thermodynamic parameters as well as on a shape of the distribution. This conclusion is coherent with the results of other studies [14,18,32,33] discussing the meaning of the $q$ index in the Tsallis approach.

Our results suggest that a similar mapping can be expected for other systems which are out of the thermodynamic equilibrium (at least in its traditional meaning). Then the problem involves additional relevant quantities, related to a deviation from the conventional equilibrium. For instance, the deviation could be induced by the heat bath properties [15], by fluctuations of intensive thermodynamic parameters [18], or by finite sizes (no thermodynamic limit) [38].

It should be emphasized that the non-additive nature of the system discussed here does not depend on the approximations made. From the every formulation of the problem we have two entropies $S_T$ and $S_R$. If we consider a "total" entropy $\Omega$ as a measure of our uncertainty on the system state, then it is clear that $\Omega$ cannot be written as an additive combination of $S_T$ and $S_R$ because these two are not independent. Therefore it would be interesting to find a way of solving this more general problem without introducing model arguments.

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[1] C. A. Tsallis, J. Stat. Phys. 52, 479 (1988)
[2] A periodically updated bibliography can be found at http://tsallis.cat.cbpf.br/biblio.htm
[3] H. Spohn, J. Phys. (France) I 3, 69 (1993)
[4] C. Tsallis, D. J. Bukman, Phys. Rev. E, 54, R2197 (1996)
[5] E. T. Jaynes, Phys. Rev. 106, 620 (1957)
[6] H. Touchette, Physica A 305, 84 (2002)
[7] E. M. F. Curado, C. Tsallis, J. Phys. A, 24, L69 (1991)
[8] C. Tsallis, R. S. Mendes, A. R. Plastino, Physica A, 261, 534 (1998)
[9] A. Renyi, Probability theory (Amsterdam: North Holland, 1970)
Here we do not discuss the problems of the replica theory itself, such as the limiting procedure or the replica symmetry breaking.