

Heat capacity and entanglement

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Summary. — Starting from a recent result on thermodynamic equilibrium of quantum systems, a connection between thermal properties, originating from Gibbs state probabilistic structure, and quantum correlations is discussed as a consequence of entanglement monogamy. As an example, a simple two-qubit system is analyzed, allowing for an expression of such a connection as an explicit function linking heat capacity to a measure of bipartite entanglement.

PACS 03.65.Aa – Quantum systems with finite Hilbert space.

PACS 03.67.Mn – Entanglement measures, witnesses, and other characterizations.

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1. – Introduction

In these last years the possibility of experimental access to mesoscopic and microscopic systems [1, 2] has triggered a strong interest in the study of properties of physical systems in connection to their quantum nature. Theoretical and experimental research on the so-called quantum thermodynamics [3], in particular, has opened new horizons while investigating the limits of applicability and the possible generalizations to quantum systems of concepts characterizing classical thermodynamics. In particular, one of the most exploited quantum features is the existence of quantum correlations [4] inside a physical system or between the system itself and the environment it interacts with. In view of the huge interest towards entanglement, an understanding of its features and its connection to thermal properties of matter [5] is a growing challenge, both because such a research might supply experimental protocols aimed at measuring entanglement (which up to now has always been experimentally elusive) and because it may highlight the fundamental, quantum origin of thermal features.

Indeed the possibility of using thermodynamic quantities, like, *e.g.*, internal energy or heat capacity, as entanglement witnesses has been shown in the case of spin systems [6],

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where a threshold on the value of these quantities exists for quantum correlations to be present in the state of the system under scrutiny. Such a connection has strong consequences in the Quantum Phase Transition (QPT) phenomenon [7]. In correspondence to a QPT, indeed, quantum correlations show some critical behavior, somehow traceable back to critical behavior of observables characterizing the system undergoing the transition. It has been shown [8] that there exist conditions under which a critical behavior of some entanglement quantifier is a necessary and sufficient condition for the occurrence of a QPT.

Finally, quite recently, non-classical correlations have been connected to the structure of thermal equilibrium itself [9]. The origin of the equilibrium Gibbs state for a small system interacting with a bath has indeed been studied in a quantum systems framework. It has been found that such a mixed state for the small system can be obtained, with a very small statistical error, from a pure state of the system + bath picked at random inside the suitable energy shell. In view of this, there is no need to start from a mixed (microcanonical) state of a composite system to obtain the thermal statistics for a part of it. The lack of knowledge leading to a mixed state for the reduced density matrix originates from the existence of quantum correlations inside the composite system.

For all these reasons, a study of the link between entanglement and thermodynamics represents a challenge of great interest both for quantum information theory and for many-body properties and condensed matter systems.

This paper is organized as follows: in sect. **2** a short introduction to a recent result [9] is given, and as a consequence some hypotheses are discussed in terms of thermodynamical properties of quantum systems. In sect. **3**, to exemplify our hypothesis, a very simple model consisting of two thermalized qubits interacting with each other via a Heisenberg-like exchange potential is studied. Section **4** is devoted to the presentation of the main result of the paper, namely an analytic function expressing the link between a measurable thermodynamical quantity and some entanglement measure, followed by some comments and conclusive remarks.

2. – Considerations on thermal equilibrium of quantum systems

As a starting point, let us briefly recall a fundamental result on quantum thermalized systems [9]: let us consider a physical system living in an n -dimensional Hilbert space \mathcal{H}^n ($n \gg 1$) and let us formally divide it into a “thermal bath” B (with Hamiltonian H_B) and a “small system” S (Hamiltonian H_S). Such a bipartition might be physically motivated by additional conditions characterizing the total system or might be completely formal. Let us anyway suppose the thermal bath (l -dimensional Hilbert space \mathcal{H}_B^l) and the system (d -dimensional Hilbert space \mathcal{H}_S^d , with $n = ld$) to be weakly coupled which each other, and moreover we choose B in such a way that $l \gg d$. If all these requirements are fulfilled it is meaningful to speak about temperature of the small system S when the total system $S + B$ is in a microcanonical ensemble $\varepsilon_R = \frac{1}{n_R} \mathcal{I}_R$ at energy E . Such an ensemble is described by a maximally mixed state in the subspace $\mathcal{H}_R^{n_R}$ of dimension n_R , obtained as the restriction of the total Hilbert space \mathcal{H}^n to a fixed energy shell. In other words, as usual, the microcanonical ensemble is the one describing an ergodic spanning of the whole energy shell. It is well known that in this case the reduced state of S is described by the canonical ensemble, characterized by the mixed state $\Omega_S = \frac{1}{Z} e^{-\beta H_S}$.

In [9] it has been shown that, supposing the total system to be in a pure state $|\Psi\rangle \in \mathcal{H}_R^{n_R}$, obtained as a coherent superposition of degenerate energy eigenstates, and tracing out the bath degrees of freedom, the probability of obtaining a reduced state

ρ_S of S sensibly different from Ω_S exponentially goes to zero with the dimension of the energy shell. In particular they have shown that

$$(1) \quad \text{Prob}\left\{\|\rho_S - \Omega_S\|_1 > \epsilon d\right\} < 2d^2 e^{-Cn_r \epsilon^2},$$

where C is a positive constant and $\|\cdot\|_1$ is the trace norm. Therefore, with a very small statistical error, we are entitled to consider the thermal state of S as originating from a partial trace operation on a pure state of the total system. The lack of knowledge about the state of S , due to which its density matrix is in general mixed, is then entirely caused by quantum correlations between S and its thermal bath.

In view of this result, one might think about a possible connection between thermal properties of a system in equilibrium (directly originated from the probabilistic structure of the mixed state Ω_S) and quantum correlations (which as shown may be considered as the cause of such a probabilistic structure). Indeed quantum correlations are known to be monogamic [10] (even if some violation to monogamy rules has been derived [11]), originating a link between the external correlations the system S can create with its thermal bath, which are the ones involved in the above-mentioned results, and internal quantum correlations between two or many subparts of the system itself. Summarizing, then, this link enables us to think about a possible relation between this latter kind of quantum correlations and measurable properties of the system.

Suppose for example that

$$(2a) \quad H_S|i\rangle = E_i|i\rangle,$$

$$(2b) \quad E_i - E_j = \omega_{ij},$$

where $i, j = 1, \dots, d$ and ω_{ij} is either finite or zero. As discussed previously, it is meaningful to consider the small system S to be in a thermal state given by

$$(3) \quad \rho_S = \rho = \frac{1}{Z} e^{-\beta H_S} = \frac{1}{Z} \sum_{i=1}^d e^{-\beta E_i} |i\rangle\langle i|$$

while the total system $S+B$ is in a state $\rho_{S+B} = |\Psi\rangle\langle\Psi|$, where as said $H|\Psi\rangle = E_{\text{tot}}|\Psi\rangle$. Of course, by definition,

$$(4) \quad \text{Tr}_B \rho_{S+B} = \rho_S.$$

Equation (4) together with $\rho_{S+B}^2 = \rho_{S+B}$ implies that the purity of ρ can reliably be used to define a measure of entanglement between the small system and the bath, since it is closely related to quantum entropies of the reduced state [4]. In particular we can define the entanglement $S-B$ as $P_E = 1 - \text{Tr}\rho^2$. Exploiting the assumption of discreteness on the energy spectrum and the form of the state of S (3) it is straightforward to show that

$$(5) \quad P_E = \frac{Z^2 - \sum_i e^{-2\beta E_i}}{Z^2} = \sum_{i \neq j} P_E^{ij},$$

where we have defined $P_E^{ij} = \frac{e^{-\beta(E_i+E_j)}}{Z^2}$ and the $\sum_{i \neq j}$ ranges over all values $i = 1, \dots, d$ and $j = 1, \dots, d$ with the constraint $i \neq j$. It is then possible to see how the mixedness of thermal states is given as a sum of individual and independent contributes from each couple of (different) energy eigenvalues.

We want now to connect such a parameter to some measurable quantity for S . Exploiting the (formal) knowledge of the partition function it is possible to obtain an expression for the heat capacity C_V of the system, which reads

$$(6) \quad C_V = \beta^2 (\langle H^2 \rangle - \langle H \rangle^2) = \beta^2 \sum_{i \neq j} P_E^{ij} \Delta_{ij}^2$$

where $\Delta_{ij}^2 = \frac{(E_i - E_j)^2}{2}$.

There is thus a strict analogy between the expression of the parameter P_E and the form of C_V . Indeed, they both are expressed as a sum over $i \neq j$ of terms depending on each possible couple of energy levels of the small system. A closer look at (6) shows that each of these contributions for C_V has the form

$$(7) \quad C_V^{ij} = P_E^{ij} \frac{\Delta_{ij}^2}{k_B T^2} = P_E^{ij} \frac{(E_i - E_j)^2}{2k_B T^2}$$

highlighting how heat capacity resembles a mixedness of the state, viewed in terms of its energy content. We can identify two different contributions in C_V^{ij} : the first one, P_E^{ij} , is related to the degree of mixedness the couple of levels $\{E_i, E_j\}$ produce in the state ρ . Second, the contribution each couple of levels gives to heat capacity depends on how distinguishable the states are in energy with respect to the mean value of thermal energy: a couple of degenerate energy levels gives no contribution to heat capacity.

In this sense, purity and heat capacity are closely related, both measuring how mixed a state is, the former from a statistical point of view and the latter from an energetic point of view.

The key point now is to turn our attention to the meaning the parameter P_E assumes in a quantum context. Indeed, as already pointed out, this parameter measures the entanglement between the small thermalized system S and the thermal bath B . In particular when $P_E = P_E^{\max} = \frac{d-1}{d}$ the bath and the system are maximally entangled, while when $P_E = 0$ the total state $|\Psi\rangle$ is factorized with respect to the bipartition (S, B) [12]. Since by definition $P_E^{ij} \geq 0 \forall i \neq j$, the only way to obtain a zero P_E is to have $P_E^{ij} \sim 0 \forall i \neq j$, thus implying $C_V \sim 0$. We can conclude that

$$(8) \quad P_E = 0 \Rightarrow C_V = 0.$$

From a physical point of view this means that each time the system is pure (being in a thermal state) it must be in a Hamiltonian eigenstate, thus resulting in no energy uncertainty and leading to a zero heat capacity.

The next step is now to link the mixedness of the state to the entanglement the small system S exhibits with respect to a possible bipartition into subsystems S_1 and S_2 . Indeed we expect such a link to be fairly strong thanks to entanglement monogamy which ensures that, as long as system and bath are entangled, there cannot exist maximal entanglement inside the system itself [10]. Vice versa, when a bipartition of the system is found to be in a maximally entangled state, the system and the bath have to be in a separable state. Thus, calling $e_{1,2}$ any bipartite entanglement measure on S , it follows that

$$(9) \quad e_{1,2} = \max \Rightarrow P_E = 0 \Rightarrow C_V = 0.$$

On the basis of these motivations, we then expect some relation exists between C_V and $e_{1,2}$, of which eq. (9) is a general feature.

3. – The two-qubit system case

To exemplify our statement, and check whether an explicit link between a measure of quantum correlations and an experimentally accessible quantity can be given in a simple case, consider a two-qubit thermalized system with Hamiltonian

$$(10) \quad H = -\frac{\lambda}{2}(\sigma_1^x \sigma_2^x + \sigma_1^y \sigma_2^y) - \frac{h}{2}\sigma^z,$$

where the coupling λ describes an exchange interactions between the two spins, h is an external magnetic field in the z -direction, $\vec{\sigma}_1$ ($\vec{\sigma}_2$) is the vector whose components are Pauli matrices for the first (second) atom and $\vec{\sigma} = \vec{\sigma}_1 + \vec{\sigma}_2$.

Its diagonalization is straightforward, since (10) is diagonal in the coupled basis $\{|S, M\rangle\} = \{|1, 1\rangle, |1, 0\rangle, |1, -1\rangle, |0, 0\rangle\}$ of common eigenvectors of S^2 and S_z , having defined $\vec{S} = \frac{\vec{\sigma}}{2}$.

In this ordered basis H reads

$$(11) \quad H = \begin{pmatrix} -h & 0 & 0 & 0 \\ 0 & -\lambda & 0 & 0 \\ 0 & 0 & h & 0 \\ 0 & 0 & 0 & \lambda \end{pmatrix}.$$

3.1. Thermal state and its properties: entanglement and heat capacity. – The diagonalization of (10) allows us to evaluate the partition function Z of the system,

$$(12) \quad Z = 2 \cosh(\beta h) + 2 \cosh(\beta \lambda),$$

where $\beta = \frac{1}{T}$ and $k_B = 1$.

Thanks to eq. (12) we are able to derive an expression for the heat capacity, which reads

$$(13) \quad \frac{C_V}{\beta^2} = \frac{h^2 + \lambda^2 + \frac{1}{2}(\lambda - h)^2 \cosh(\beta(\lambda + h)) + \frac{1}{2}(\lambda + h)^2 \cosh(\beta(\lambda - h))}{(\cosh(\beta h) + \cosh(\beta \lambda))^2}.$$

The other quantity we are interested in is a parameter measuring quantum correlations established between the two spins. The most common entanglement measure to characterize correlations between qubits is the so-called concurrence [13], defined as $\mathcal{C} = \text{Max}\{0, \nu\}$, where $\nu = \sqrt{\mu_1} - \sqrt{\mu_2} - \sqrt{\mu_3} - \sqrt{\mu_4}$. Here the μ_i 's are eigenvalues of the matrix $\rho(\sigma_y \otimes \sigma_y) \rho^*(\sigma_y \otimes \sigma_y)$ and $\mu_1 \geq \mu_2 \geq \mu_3 \geq \mu_4$, ρ being in our case the thermal Gibbs state $\frac{1}{Z} e^{-\beta H}$. Recall that \mathcal{C} is zero for separable states, while it goes to 1 for maximally entangled states.

After some trivial calculations we can give an explicit expression for the concurrence, which reads

$$(14) \quad \mathcal{C} = \text{Max} \left\{ 0, \nu = \frac{2}{Z} (|\sinh \beta \lambda| - 1) \right\}.$$

Some interesting features can be noticed closely analyzing eq. (14). Strictly speaking, indeed, the system in its thermal state is entangled if and only if $|\lambda| > \frac{1}{\beta} \ln(1 + \sqrt{2}) = \bar{\lambda}$, which is, surprisingly, a value independent of h . However, notice that in (14) the partition function explicitly depends upon h , in such a way that when $h \gg \lambda$, $Z \gg |\sinh \beta\lambda| - 1$ so that $\mathcal{C} \sim 0$. Only when λ is at least of the same order of h entanglement can exist in the system, since otherwise the magnetic interaction destroys any possible correlation between spins.

Equation (14) depends on the three parameters β, λ and h , and the same parameters enter the expression for C_V . Consider now h as a parameter characterizing a class of functions $\mathcal{C}_h(\beta, \lambda)$. In this way we can reduce the number of variables in \mathcal{C} , being able to handle it analytically, as shown in the next section.

4. – Explicit link: heat capacity from concurrence

Equation (14) allows us to obtain a class of inverse functions parameterized by h where λ plays the role of dependent variable, in terms of β and ν . To this end we write

$$(15) \quad C_h = \text{Max} \left\{ 0, \nu = \frac{1}{\cosh \beta h + \sqrt{1 + \sinh^2 \beta \lambda}} (|\sinh \beta \lambda| - 1) \right\}.$$

Note now that (14) is an even function of λ , so that we can limit ourselves to $\lambda \geq 0$. Set now $x = \sinh \beta \lambda$ and $a = \cosh \beta h$ and write for ν :

$$(16) \quad \nu = \frac{x - 1}{a + \sqrt{1 + x^2}}.$$

It is then straightforward to obtain

$$(17) \quad \lambda_h(\nu, \beta) = \frac{1}{\beta} \text{ArcSinh} \left(\frac{a\nu + 1 + \nu \sqrt{(a\nu + 1)^2 + 1 - \nu^2}}{1 - \nu^2} \right).$$

This is a continuous function of ν in its domain $D = [-\frac{1}{a+1}, 1]$. However, recall that the only physical values of ν are the ones in $[0, 1]$, where (17) actually describes the exact dependence of λ upon \mathcal{C} . It is easy to see, however, that when $\lambda \in [0, \frac{1}{\beta} \ln(1 + \sqrt{2})]$ the concurrence is not an invertible function of λ since in these cases \mathcal{C} is identically zero. In what follows, then, one must always keep in mind that for negative values of ν nothing can be said about the relation between entanglement and thermodynamic quantities, since the former is always zero.

Having at our disposal the function (17), we can explicitly introduce the parameter ν into the expression for heat capacity by substituting (17) in (13), thus obtaining the set of functions $C_V^{(h)}(\beta, \nu)$

$$(18) \quad C_V^{(h)}(\beta, \nu) = \frac{\beta^2}{(a + \cosh(\beta \lambda_h(\nu, \beta)))^2} \left(\frac{1}{2} (\lambda_h(\nu, \beta) - h)^2 \cosh(\beta(\lambda_h(\nu, \beta) + h)) + \frac{1}{2} (\lambda_h(\nu, \beta) + h)^2 \cosh(\beta(\lambda_h(\nu, \beta) - h)) + h^2 + \lambda_h^2(\nu, \beta) \right).$$

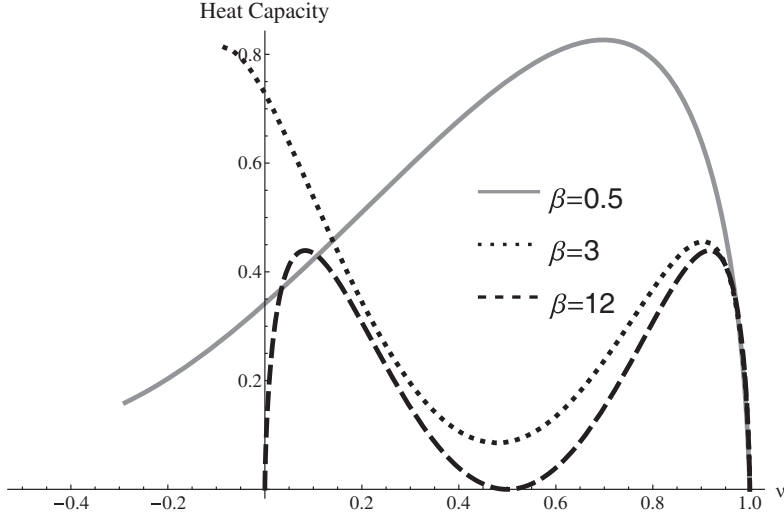


Fig. 1. – Heat capacity C_V of the system *vs.* ν (all energies are measured in units of magnetic field h) for 3 different values of β : $\beta = 0.5$ (solid line), $\beta = 3$ (dotted line) and $\beta = 12$ (dashed line).

Equation (18) is our main result, providing an explicit, analytic link between a thermal parameter and an entanglement measure. It shows how, once entanglement in the system is known at fixed temperature and magnetic field, heat capacity is uniquely determined. Unfortunately, the converse is not true.

Let us closely analyze (18) in the case of strong correlations between spins. In the previous section we have argued that C_V should become negligible when entanglement approaches its maximum. Indeed, in our case

$$(19) \quad \lim_{\nu \rightarrow 1} C_V^{(h)}(\beta, \nu) = 0$$

as one can easily check using (17) and (18). To simplify calculations, in what follows we will measure all energies in units of h , thus obtaining the function $C_V^{(1)}(\beta, \nu)$. In fig. 1 such a function is shown for 3 different values of temperature.

Figure 1 highlights how heat capacity is not a monotonic function of concurrence. This means that a measure of C_V is unable to supply information about entanglement. On the other hand, the knowledge of the concurrence determines the value of C_V as long as ν is positive. The range of zero entanglement ($\nu \leq 0$) gets smaller and smaller as temperature tends to zero. In this limit the weight of quantum correlations, with respect to classical ones, grows so that any collective physical property results more and more affected by entanglement itself. In our simple case, the bouncing behavior shown in fig. 1 can be explained by a detailed analysis of the energy spectrum in parameter space, reflecting the relative strength of spin-spin interaction compared to the magnetic one, which in turn is connected to the entanglement between the two spins.

From fig. 1 we see that at low temperature ($\beta = 12$ line) heat capacity shows two maxima and a minimum between them. At such low temperature the system can be seen as an effective two-level one, since the only two occupied levels are the ground state

and, close to level crossings, the first excited one. Indeed the presence of a maximum and a minimum in heat capacity is typical of gapped two-level systems and is known as Schottky anomaly [14]⁽¹⁾. In our case, however, we are moving in parameter space keeping temperature fixed. That is why we obtain a double Schottky-like anomaly with a second maximum in a symmetric position with respect to the minimum point. Such a behavior is independent of the specific system, and characterizes any gapped system in correspondence to a level crossing in its spectrum in parameter space, when temperature is low enough. In these conditions, when the number of components of the system is statistically significant, one may speak of first-order quantum phase transitions [7]. Our analysis then suggests how, in correspondence to any first-order quantum critical point, C_V shows a typically oscillating behavior signaling the presence of a transition.

As already noticed, due to this oscillating behavior it is not possible from a single measure of C_V to infer the value of the concurrence. This is due to the fact that, depending on the value obtained after a measurement is performed, there might be many different values of ν associable to it, since as said $C_V(\nu)$ is not monotonous. In other words, keeping both h and β fixed, there might exist many different systems, physically characterized by different values of λ , showing the same heat capacity.

In [15], however, it is shown how to exploit a finite number of measures of C_V at different temperatures to determine the value of bipartite entanglement in the system.

Briefly, such an entanglement measuring protocol is based on the fact that each measured value of heat capacity corresponds to a set S_a of values of λ compatible with it. The experimentalist however does not know in advance which one among these values is the one actually exhibited by the system. Measuring C_V for different values of temperature allows one to obtain many different sets S_a, S_b, \dots, S_n . Such a procedure can be employed until the physical value of λ is uniquely identified as the only element of the set $S_a \cap S_b \cap S_c \cap \dots \cap S_n$. Finally, in view of (14), the knowledge of λ corresponds to a knowledge of the concurrence. This shows how a finite number of measurements of heat capacity of the two-qubit (10) system allows for an indirect measurement of entanglement and, actually, of any other microscopic property of the system itself.

4.1. Conclusive remarks. – The analysis performed for such a simple system confirms, on the one hand, the features discussed in sect. 2 about the connection between entanglement measures and thermal properties at equilibrium, showing how this connection might be exploited to get an insight into the role quantum correlations have in characterizing physical measurable quantities. On the other hand, such a simple example suggests that a link between entanglement and heat capacity might be stronger than previously argued [16] even for many-body systems, and that some typically quantum phenomenon such as first-order QPTs (in which entanglement plays a fundamental role) can be identified by a characteristic behavior of C_V , independently of the particular system under scrutiny.

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⁽¹⁾ A Schottky anomaly is a feature of any two-level system, for which heat capacity *vs.* temperature shows a maximum followed by an asymptotic decreasing toward zero

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