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Thermodynamic potentials for simple magnetic systems

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Abstract

A strong discrepancy of criteria appears in texts on Statistical Mechanics when associating the partition function of simple magnetic systems with thermodynamical potentials. The aim of this work is to provide an adequate description, starting from the maximization of entropy. Finally, a discussion about some thermodynamic properties is given.

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1. Introduction

There are many possibilities of expressing the entropy S of a system in thermodynamic equilibrium in terms of the corresponding probability density ρ. The expression first introduced by Gibbs [1] provides adequate results for the thermodynamic properties of most systems in equilibrium, and has therefore been used almost universally. For a classical system of N particles described by generalized coordinates and momenta $\boldsymbol{q}$ and $\boldsymbol{p}$, this expression takes the well-known form

$$S = -k \int \rho \ln(C^N \rho) \, \mathrm{d}^{3N}\boldsymbol{p} \, \mathrm{d}^{3N}\boldsymbol{q}.$$

The constant C^N is introduced in order to obtain the correct units. For quantum systems, the relationship between entropy and the probability density operator $\hat{\rho}$ becomes

$$S = -k \, \mathrm{Tr}(\hat{\rho} \ln \hat{\rho}).$$

When dealing with simple magnetic systems, the $\hat{\rho}$ operator acts on spin coordinates; if the eigenfunctions are used for constructing the operators in the previous expression, a simple sum has to be assessed. An example for magnetic systems is given by the well-known one-dimensional chain of N nuclei, whose spin coordinates can take the eigenvalues σ_i (as long as a suitable basis is chosen). If there is no interaction among the nuclei, but only with an external magnetic induction of magnitude B, the system will be governed by the following Hamiltonian eigenvalues:

$$\mathscr{H} = -\mu \sum_{i=1}^{N} B\sigma_i, \tag{1}$$

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where μ is the magnetic moment for each nucleus. Thermodynamic properties can be derived from the corresponding partition function

$$Q = \sum \mathrm{e}^{-\beta \mathscr{H}},$$

where $\beta = 1/kT$, k being the Boltzmann constant and T the temperature of the system; the summation runs over all the possible states of the system. For the present discussion, attention will be focused on the case of spin-$\frac{1}{2}$ particles. The partition function will then read

$$Q = \left(2\cosh\frac{\mu\beta B}{2}\right)^N. \tag{2}$$

This typical result appears in many text books on elementary Statistical Mechanics. Since nuclei are independent, the overall partition function was expected to read as the product of single summations q for each spin ($Q = q^N$). Usually, the partition function is associated with some thermodynamic potential ϕ by means of

$$\phi = -kT \ln Q. \tag{3}$$

Although the example chosen appears to be very simple, no agreement is shown in the literature about which thermodynamic potential corresponds to Eq. (3). For instance, some authors [2–4] suggest that ϕ is the *Helmholtz* free energy, i.e., the Legendre transformation in the internal energy U which changes S by T:

$$\phi = U - TS, \tag{4}$$

whereas others [5,6] take it as the *Gibbs* free energy, which means a further transformation involving the substitution of the total magnetization M by the external field B:

$$\phi = U - TS - BM. \tag{5}$$

Obviously, the discrepancy is not just a matter of "names" for the potential in Eq. (3), since the description of the thermodynamical properties of our system will not be the same in the two cases. However, this last association seems to be borne in mind when looking for the total magnetization of the system, even when ϕ is referred to as the Helmholtz potential, since the expression always used is

$$M = -\left(\frac{\partial\phi}{\partial B}\right)_{T,N},$$

which produces the correct result

$$M = \frac{N\mu}{2}\tanh\frac{\mu B}{2kT}. \tag{6}$$

On the other hand, most texts state that the internal energy may be computed as the mean value of Eq. (1). This may be written as

$$U \equiv \langle \mathscr{H} \rangle = -\left(\frac{\partial(\ln Q)}{\partial\beta}\right)_{B,N}, \tag{7}$$

which for the present example gives

$$U = -\frac{N\mu B}{2}\tanh\frac{\mu B}{2kT}. \tag{8}$$

In addition, if the association of Eq. (3) with the Gibbs potential is always borne in mind, an expression for the entropy can be derived

$$S = -\left(\frac{\partial\phi}{\partial T}\right)_{B,N},$$

obtaining for this system

$$S = kN\ln\left(2\cosh\frac{\mu B}{2kT}\right) - \frac{N\mu B}{2T}\tanh\frac{\mu B}{2kT}. \tag{9}$$

At this point, an apparent contradiction arises, since by simply adding $U - TS - BM$ the Gibbs potential provided by Eq. (3) is not reobtained. Although it may be thought that the error is the acceptance of ϕ as the Gibbs free energy, the reader may verify that this and even more contradictions arise if ϕ from Eq. (3) is taken as the Helmholtz free energy.

Unfortunately, text books on Statistical Mechanics pay little attention to this controversy, disencouraging an adequate comprehension of the fundamentals of the subject. This is not a minor issue, since the identification of the partition function with a thermodynamic potential must hold not only for the case of non-interacting spins. In the next section, some basic steps are reviewed in order to achieve the correct associations with thermodynamical properties.

2. Maximization of entropy and connection with thermodynamics

In order to avoid misinterpretations, the expressions for the probability distribution of the system chosen will be rederived by means of extremizing the entropy function, adequately imposing the corresponding constraints.

Since the nuclei in our system are independent, attention will be focused on one single spin. The joint probability for the whole system will be obtained by simply multiplying the probabilities for all separate nuclei. If the eigenvectors of the spin operator are taken as the basis for describing spin states, $P(i)$ represents the probability that our spin be with quantum number $\sigma_i \, (= \pm\frac{1}{2})$.

The normalization condition for these probabilities provides the first constraint that must be used

$$\sum P(i) = 1.$$

The mean value of the interaction Hamiltonian of Eq. (1) might also be chosen as a constraint. Or equivalently, since the external magnetic field remains constant, the total magnetization M must be regarded as a mean value. In the present case, the individual magnetization M_i will be taken as the second constraint

$$M_i = \mu \, \langle \sigma_i \rangle .$$

Now attention will be focused on the internal energy of our system. At first sight, it looks natural to have the internal energy as $-BM$, i.e., to accept the association of Eq. (7) as valid. As mentioned above, many texts take this association as obvious, although it is in disagreement with first principles. In order to avoid misleading ideas, it is worth starting from the combined first and second laws of thermodynamics,

$$\mathrm{d}U = T\,\mathrm{d}S + đW + \zeta\,\mathrm{d}N, \tag{10}$$

where $đW$ must represent the *external* work done on the system, ζ being the chemical potential (in this expression we assume there are no further thermodynamical parameters to describe our system). The external work of an external field B which produces a variation $\mathrm{d}M$ on a system of *total* magnetization M is given by $B\,\mathrm{d}M$—the energy for creating the field may be excluded from our system, since it has nothing to do with the thermodynamic properties in which we are interested (a very good explanation is detailed in Appendix B of Ref. [2]). Although agreement about this point is very well accepted by all the literature (see e.g., Ref. [7]), $đW$ is not always adequately written when analyzing thermodynamic properties of a magnetic system. However, once the system has clearly been defined—in our example, the set of nuclei—the expression for $\mathrm{d}W$ is not arbitrary at all. (It is worth noting that the induction field includes in fact "internal" effects, since it accounts both for the external magnetic field H and the field due to magnetization of the system under consideration. The expression *external induction* field refers to the exclusion of this magnetization term. Referring to the constitutive relation between induction and magnetic fields, the external induction is $\mu_0 H$, μ_0 being the magnetic permeability of vacuum, and not H as often considered. In addition, if $đW$ is taken as $H\,\mathrm{d}M$, inconsistencies in units may arise). The Euler relation for a magnetic system thus reads

$$U = TS + BM + \zeta N. \tag{11}$$

When a system is under the action of an external field which is held constant, it is useful to introduce the enthalpy, defined as the difference of the internal energy and a term which accounts for the coupling with the outside world. In the case of magnetic systems, it usually referred to as "magnetic enthalpy"

$$E = U - BM.$$

This is precisely the magnitude associated with the mean value of the Hamiltonian of Eq. (1): no matter the configuration of the system, the field B

will remain constant (see e.g., Ref. [8]). Although the magnetic enthalpy may not always be regarded as a Legendre transform of the internal energy (the necessary conditions are detailed in Ref. [2, p. 142]), its physical meaning is clear: it represents the internal energy of a new system, which also includes the sources of the field B. Now, if we make the adequate identification of the mean value given by Eq. (7), we have $E = -BM$, and therefore the internal energy will vanish for all temperatures and magnitudes of B. We will return to this point later.

Before carrying on, it is worth noting that if any interaction among the spins is included in the Hamiltonian of Eq. (1), all the arguments stated above will hold: the only difference in the analyisis is that the mean value of this new Hamiltonian will not look like $-BM$, and an additional constraint should appear in the next steps.

The set of probabilities which extremize the entropy restricted by the constraints mentioned above can now be obtained through the usual procedure, using Lagrange multipliers. These multipliers will be called α_0 and α_M for the normalization condition and the individual magnetization, respectively; the extremum condition then reads

$$\delta\left\{\sum[\alpha_0 P(i) - kP(i)\ln P(i) - \alpha_M P(i)\sigma_i]\right\} = 0.$$

Now, since all infinitesimal variations $\delta P(i)$ must be independent, this condition implies

$$[\alpha_0 - k - k\ln P(i) - \alpha_M\sigma_i]\delta P(i) = 0.$$

Since this equation must hold for any $\delta P(i)$, the bracket on the left-hand member must vanish:

$$\alpha_0 - k - k\ln P(i) - \alpha_M\,\sigma_i = 0. \tag{12}$$

If this equation is multiplied by $P(i)$ and summation over i is performed, the identification of the partition function per nucleus as

$$q = \sum e^{\alpha_M \mu\sigma_i/k} = e^{1-\alpha_0/k}$$

arises naturally. Eq. (12) thus becomes

$$-kT\ln q = \alpha_M TM_i - TS_i,$$

S_i being the entropy per nucleus. Following the usual arguments (see e.g., Ref. [5]), in this equation, the right member can be associated with a thermodynamic potential, since the first term is related to the enthalpy $-BM$ if the identification $\alpha_M = -B/T$ is allowed. Then, for the whole system this may be written as

$$-kT\ln Q = U - TS - BM, \tag{13}$$

confirming the identification with the Gibbs potential, as suggested in Eq. (5), is the correct one. As stated above, when some kind of interaction among spins is present, U will not vanish, but Eq. (13) will still be valid.

3. Discussion

Now that the partition function has adequately been associated with Gibbs free energy, we should be able to verify some thermodynamic properties for our system. First, we will return to Eq. (13): the term U in the right-hand side has been deliberately introduced here in order to emphasize the fact that the internal energy vanishes for this system. Is this a reasonable idea? Unlike other physical situations, this system is built up by elements which interact with an external field but without "absorbing" this interaction energy for themselves. A comparison may be done with an ideal gas, i.e., a system of non-interacting point mass particles within a rigid cylinder with a free piston at one end: the external field is the pressure which performs mechanical work on the system when volume changes occur. The particles absorb this work, converting it into kinetic energy, which will not disappear when the external pressure vanishes. If the reader is not acquainted with this example, he is invited to carry out the maximization of the entropy bearing in mind that instead of the volume, it is the pressure that is held constant, which again implies the correspondence of the partition function and the Gibbs free energy. The usual form of the Hamiltonian for free particles takes into account the energy which is effectively absorbed by the particles, which allows a better comprehension of the association of $-kT\ln Q$ with the Gibbs free energy. In our spin system, however, when the magnetic field disappears, no energy can be maintained in the nuclei. Thus, the fact that the internal energy vanishes is indeed a reasonable idea; however, Eq. (11) may not be considered as a "fundamental equation", since not all partial derivatives of U make sense and therefore, it is not possible to draw all thermodynamic properties of the system from this equation alone [9].

A further comment can be stated about this null internal energy. From Eq. (9), the heat capacities can be assessed; they provide an idea about the capability of our spin system for absorbing energy by heat transfer. In the case of the heat capacity at constant field H (or constant external induction B), a simple derivative produces the well-known result

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_{B,N} = \frac{(\mu B)^2 N}{4kT^2}\,\mathrm{sech}^2\,\frac{\mu B}{2kT}. \tag{14}$$

The capability of absorbing heat from a thermal reservoir when the field is held constant obviously depends on the source of B, which must provide energy so that the system changes its magnetization when changes of temperature occur. This would suggest that no energy is necessarily absorbed by the system when heat interchanges occur, but it may be transferred to the sources of B. In fact, this can be checked by simply applying Eq. (10) for a process in which B and N are maintained constant; the variation of U with T must therefore obey the well-known identity

$$\left(\frac{\partial U}{\partial T}\right)_{B,N} = C_H + B\left(\frac{\partial M}{\partial T}\right)_{B,N}.$$

The right-hand member of this equation vanishes, as can be verified easily by combining Eqs. (6) and (14). This precisely confirms the fact that, although C_H is not zero, the system does not absorb energy when heat interchanges occur at constant B. On the other hand, an expression for the heat capacity C_M at constant magnetization may also be derived. With M given by Eq. (6), the expression for S of Eq. (9) may be rewritten in terms of T, M, and N, obtaining

$$S(T, M, N) = \frac{kN}{2}\ln\left[\frac{4}{1-(2M/\mu N)^2}\right] - \frac{2kM}{\mu}\,\mathrm{arctanh}\,\frac{2M}{\mu N}.$$

Since S is not explicitly dependent on T, the heat capacity at constant magnetization will be identically zero: this coincides with the fact that $C_M = (\partial U/\partial T)_{M,N}$, enhancing the conclusions drawn above. An alternative way to see that C_M should vanish is to recall that heat capacities must be related by

$$\begin{aligned} C_M &= C_H + T\left(\frac{\partial M}{\partial T}\right)_{B,N}\left(\frac{\partial B}{\partial T}\right)_{M,N} \\ &= C_H - T\frac{(\partial M/\partial T)^2_{B,N}}{(\partial M/\partial B)_{T,N}}. \end{aligned}$$

The right-hand member of this expression can be computed using Eqs. (14) and (6), reobtaining a null value for C_M.

4. Conclusion

Care has been taken in the derivation of thermodynamical properties of a non-interacting spin-$\frac{1}{2}$ system from basic Statistical Mechanics. A correct association of the partition function with Gibbs free energy has been achieved, reobtaining well-known formulae for the entropy S and the total magnetization M. On the other hand, the improper identification of the internal energy U with the mean value of the interaction Hamiltonian has been overcome, replacing it by the magnetic enthalpy. It has been shown that in fact, these associations of thermodynamic potentials are valid also for magnetic systems with non-null interaction among spins.

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