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Statistical mechanics of few-particle systems: exact results for two useful models

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Abstract

The statistical mechanics of small clusters ($n \sim 10$ –50 elements) of harmonic oscillators and two-level systems is studied exactly, following the microcanonical, canonical and grand canonical formalisms. For clusters with several hundred particles, the results from the three formalisms coincide with those found in the thermodynamic limit. However, for clusters formed by a few tens of elements, the three ensembles yield different results. For a cluster with a few tens of harmonic oscillators, when the heat capacity per oscillator is evaluated within the canonical formalism, it reaches a limit value equal to k_B , as in the thermodynamic case, while within the microcanonical formalism the limit value is $k_B(1-1/n)$. This difference could be measured experimentally. For a cluster with a few tens of two-level systems, the heat capacity evaluated within the canonical and microcanonical ensembles also presents differences that could be detected experimentally. Both the microcanonical and grand canonical formalism show that the entropy is non-additive for systems this small, while the canonical ensemble reaches the opposite conclusion. These results suggest that the microcanonical ensemble is the most appropriate for dealing with systems with tens of particles.

Keywords: few-particle systems, ensembles, specific heat nanoparticles

(Some figures may appear in colour only in the online journal)

1. Introduction

Statistical mechanics has traditionally dealt with systems formed by a large number of particles ($n \sim 10^{23}$); but, at present, experiments can be carried out on clusters with a few tens of

atoms [1]. This justifies studying the statistical mechanics of systems with few particles and low energy, and one may even wonder about the equivalence of the different formalisms when the system is small. Conventional wisdom [2–4] states that the results obtained with the microcanonical, canonical and grand canonical formalisms coincide in the thermodynamic limit. However, it is known that no such thing occurs in certain situations, which has generated an active line of research [5–7]. The examination of such cases has been focused on models with theoretical interest but with very limited use for modelling experiments. For this reason, the current paper proposes the study of two models widely used to analyse experimental results: the harmonic oscillator and the two-level system, which can also be interpreted as a spin system. The objective here is to evaluate exactly the statistical mechanics for these two models when they have few particles and, consequently, low energy. This implies keeping in mind that the energy is quantised, i.e., that the system has an integer number of energy quanta. Thus, the idea is to calculate statistical properties in terms of the fundamental constituents of the system: the number of matter particles n and the number of energy quanta m , using the three usual formalisms of statistical mechanics.

In previous publications [8, 9] some results in this direction were obtained. In this article the three usual formalisms of statistical mechanics are considered and it is shown that exact analytic expressions for thermodynamics magnitudes can be found. This is an interesting and instructive exercise for a graduate course in statistical physics; exact results are always attractive. And an intriguing question is stated: for systems with few tens of particles, the canonical and microcanonical formalisms lead to different results that might be observable in experiments. Perhaps someone might try to find out which formalism is the right one.

This article is structured as follows: in section 2 the models are described and analysed within the microcanonical formalism; in section 3 the harmonic oscillator and the two-level system are analysed within the canonical formalism; in section 4 the relationship between the canonical and grand canonical formalisms is discussed, and the models are analysed with the latter; in section 5 results are compared and discussed; and in section 6 some final remarks are made.

2. Models within the microcanonical ensemble

As already mentioned, the goal of this article is to analyse two models, widely used throughout the literature, when they are formed by few particles n . Due to such size, the discrete nature of energy must be taken into account and, therefore, the studied system should be considered to have m energy quanta. For a system consisting of n harmonic oscillators with a frequency ν , the energy is expressed:

$$E = m h \nu. \quad (1)$$

Note that the zero-point energy of the oscillators has not been taken into account. To include it, a term $n \frac{1}{2} h \nu$ should be added to (1), but this has no observable consequences. From here onwards, the units used will be such that $h \nu = 1$. Thus, the energy is simply the number of quanta present. In this article, entropy is measured in such units such that $k_B = 1$.

The microcanonical entropy of n oscillators with m energy quanta is [3]:

$$S_{\text{osc}}(n, m) = \ln \left[\frac{(m+n-1)!}{m!(n-1)!} \right]. \quad (2)$$

It is convenient to rewrite (2) avoiding factorials. The usual treatment for this problem is to use Stirling's approximation, which is valid for large systems. However, the systems studied in this article have small n and m , so that a rewritten version of the exact expression (2) will be used here. To rewrite the formula, it should be kept in mind that: $\ln[x!] = \sum_{k=1}^x \ln[k]$. Using this expression for the three factorials that appear in (2) and doing some algebraic manipulations, that equation can be rewritten as:

$$S_{\text{osc}}^{\text{mic}}(n, m) = \sum_{k=1}^m \ln \left[\frac{k+n-1}{k} \right]. \quad (3)$$

Note that expression (3) is exact, includes no approximations, and is, therefore, appropriate for dealing with systems with small n and m . Superscript 'mic' indicates that the oscillator's entropy is evaluated within the microcanonical formalism.

The next step is to obtain the temperature for the cluster of oscillators. This is done through the well-known thermodynamic expression: $1/T = (\partial S / \partial E)_n$. However, it must be kept in mind that the energy is quantised. As the system has $m, m-1, m-2$, etc., energy quanta, the derivative cannot be calculated and the expression must be rewritten using finite differences. The resulting equation is:

$$\frac{1}{T} = S(n, m) - S(n, m-1). \quad (4)$$

A backward finite difference scheme was used for the temperature to be properly defined even when $m = 0$. By using this scheme, it can be verified that $T(m) \rightarrow 0$ when $m \rightarrow 0$. If a forward difference scheme is used, the temperature differs from zero when there are no energy quanta, which is physically incorrect.

From (2) and (4), it follows that the temperature for the oscillator in the microcanonical ensemble is:

$$\frac{1}{T_{\text{osc}}^{\text{mic}}} = \ln \left[\frac{m+n-1}{m} \right]. \quad (5)$$

It is easy to verify that $T_{\text{osc}}^{\text{mic}} \rightarrow 0$ when $m \rightarrow 0$, as expected.

To calculate the chemical potential, the expression used is: $\mu/T = -(\partial S / \partial n)_E$. Again, given that the number of particles is discrete, the derivative must be replaced by finite differences:

$$\mu = -\frac{S(n, m) - S(n-1, m)}{S(n, m) - S(n, m-1)}. \quad (6)$$

From (2), (5) and (6), it follows that:

$$\mu_{\text{osc}}^{\text{mic}} = -\ln \left[\frac{m+n-1}{n-1} \right] / \ln \left[\frac{m+n-1}{m} \right]. \quad (7)$$

To calculate the heat capacity, remember $C = (\partial E / \partial T)_n$. Once again, considering that the energy only assumes discrete values, the smallest possible change for E is 1, i.e., a system with m quanta now has $(m+1)$ quanta. Thus, the resulting expression to calculate the heat capacity is:

$$\frac{1}{C} = T(n, m + 1) - T(n, m). \quad (8)$$

It should be noted that, in this case, a forward difference scheme was used, due to what occurs when $m \rightarrow 0$. For oscillators as well as for two-level systems, if a backward difference scheme is used, then $C \rightarrow -\ln[-2 - n]$, i.e., the heat capacity becomes imaginary. When a forward difference scheme is used, then $C \rightarrow \ln[n]$ for both models.

For the harmonic oscillator, from (5) and (8) it follows that:

$$C_{\text{osc}}^{\text{mic}} = \ln\left[\frac{m+n}{1+m}\right] \ln\left[\frac{m+n-1}{m}\right] / \ln\left[\frac{(n+m-1)(m+1)}{m(n+m)}\right]. \quad (9)$$

The same type of calculations can be applied to clusters formed by n two-level systems, where each object can be in a ground state with energy 0 and an excited state with energy ε . Clearly, this could be considered as spins in a magnetic field where the zero of energy corresponds to the situation in which the spin is parallel to the field. If there are m particles in an excited state, this means that there are m energy quanta, i.e.:

$$E = m\varepsilon. \quad (10)$$

As in the case of the oscillator, the energy and entropy are measured in such units that $\varepsilon = 1$ and $k_B = 1$. The microcanonical entropy for the two-level system is given by [3]:

$$S_{\text{two}}^{\text{mic}} = \ln\left[\frac{n!}{m!(n-m)!}\right]. \quad (11)$$

Like in the previous case, it is convenient to write factorials as logarithmic summations; reordering terms, the resulting expression is:

$$S_{\text{two}}^{\text{mic}} = \sum_{k=1}^{n-m} \ln\left[\frac{k+m}{k}\right]. \quad (12)$$

From (4) and (11), it follows that the microcanonical temperature is:

$$\frac{1}{T_{\text{two}}^{\text{mic}}} = \ln\left[\frac{n-m+1}{m}\right]. \quad (13)$$

The chemical potential is obtained from (6) and (11):

$$\mu_{\text{two}}^{\text{mic}} = \ln\left[\frac{n-m}{n}\right] / \ln\left[\frac{n-m+1}{m}\right]. \quad (14)$$

Finally, the heat capacity is obtained from (8) and (13):

$$C_{\text{two}}^{\text{mic}} = \ln\left[\frac{n-m+1}{m}\right] \ln\left[\frac{n-m}{m+1}\right] / \ln\left[\frac{(n-m+1)(m+1)}{m(n-m)}\right]. \quad (15)$$

This section thus concludes with the calculations within the microcanonical formalism. Entropy, temperature, chemical potential and heat capacity have been expressed for a system formed by quantum harmonic oscillators—equations (3), (5), (7) and (9)—and for a cluster of two-level systems—equations (12)–(15). Results are exact, without approximations of any kind. The next step is analysing these two models within the canonical ensemble and expressing the relevant thermodynamic properties in terms of n and m .

3. Canonical formalism

This section deals first with the harmonic oscillator within the canonical formalism. It is known that the partition function of an oscillator in contact with a thermal bath at temperature T is [2–4]:

$$Z_{\text{osc}} = \frac{1}{1 - e^{-1/t}}. \quad (16)$$

If the oscillators are considered distinguishable (e.g., because they are fixed in a crystal lattice), then the partitioning function of the cluster is: $Z = (Z_{\text{osc}})^n$. The energy can be calculated as [2–4]: $E = T^2 (\partial \ln Z / \partial T)$. And, consequently, the mean energy per oscillator \bar{E} is:

$$\bar{E}^{\text{can}} = \frac{1}{e^{1/T} - 1} = \frac{m}{n}. \quad (17)$$

This gives:

$$T_{\text{osc}}^{\text{can}} = 1 / \ln \left[\frac{n+m}{m} \right]. \quad (18)$$

This is the canonical temperature (indicated with superscript ‘can’) for the cluster of oscillators, expressed in terms of system constituents, i.e., the n particles and the m quanta. This expression should be compared with equation (5).

The chemical potential in the canonical ensemble is obtained from: $\mu = -(\partial (T \ln Z) / \partial n)_E$, which gives:

$$\mu_{\text{osc}}^{\text{can}} = - \ln \left[\frac{m+n}{n} \right] / \ln \left[\frac{m+n}{m} \right]. \quad (19)$$

This expression is analogous to equation (7).

For the entropy calculation, one should remember [3, 4] the relationship between the partition function, the Helmholtz free energy F and the entropy: $S = -\partial F / \partial T = \partial (T \ln Z) / \partial T = \ln Z + T (\partial \ln Z / \partial T)$. Then:

$$S_{\text{osc}}^{\text{can}} = n \ln \left[\frac{n+m}{n} \right] + m \ln \left[\frac{n+m}{m} \right]. \quad (20)$$

Finally, the heat capacity of the oscillators cluster evaluated in the canonical ensemble is:

$$C_{\text{osc}}^{\text{can}} = \frac{m}{n} (m+n) \left(\ln \left[\frac{n+m}{m} \right] \right)^2. \quad (21)$$

Next, let us evaluate a cluster formed by two-level systems within the canonical formalism. The partition function for one of this object is [2, 3]:

$$Z_{\text{two}} = 1 + e^{-1/T}. \quad (22)$$

It follows that the mean energy \bar{E} of the particle is:

$$\bar{E}^{\text{can}} = (1 + e^{-1/T})^{-1} = \frac{m}{n}. \quad (23)$$

Once again, the mean energy is equal to m/n ; and the temperature, expressed in terms of the fundamental constituents of the system, can be evaluated within the canonical ensemble thus:

$$T_{\text{two}}^{\text{can}} = 1 / \ln \left[\frac{n-m}{m} \right]. \quad (24)$$

From this point onwards, the same formulas used for the harmonic oscillator apply here, using (24) to replace the temperature. Thus, for a cluster consisting of n two-level systems with m energy quanta, the following expressions are valid:

$$\mu_{\text{two}}^{\text{can}} = \ln \left[\frac{n-m}{n} \right] / \ln \left[\frac{n-m}{m} \right], \quad (25)$$

$$S_{\text{two}}^{\text{can}} = n \ln \left[\frac{n}{n-m} \right] - m \ln \left[\frac{m}{n-m} \right], \quad (26)$$

$$C_{\text{two}}^{\text{can}} = \frac{m}{n} (n-m) \left(\ln \left[\frac{n-m}{m} \right] \right)^2. \quad (27)$$

In the next section, the models are analysed within the grand canonical formalism.

4. Grand canonical formalism

The canonical and grand canonical formalisms are closely related, so much so that the physical properties calculated within the grand canonical formalism can be expressed in terms of the same properties evaluated within the canonical formalism. These relationships are briefly mentioned as follows.

The grand partition function \mathcal{Z} is connected to the canonical partition function Z through [3, 4]:

$$\mathcal{Z}(T, \mu) = \sum_{n=0}^{\infty} e^{n\mu/T} Z(T, n) = \sum_{n=0}^{\infty} e^{n\mu/T} Z_1(T)^n = 1 / (1 - e^{\mu/T} Z_1(T)). \quad (28)$$

Z_1 is the partition function of a single object. In this case, it will be either Z_{osc} given by (16) or Z_{two} given by (22). The properties that are relevant to this work can be obtained from equation (28) and using the usual formulas of the grand canonical ensemble [2–4]:

$$E^{\text{gca}} = -T^2 \left(\frac{\partial \ln \mathcal{Z}}{\partial T} \right)_{\mu/T} = nT^2 \frac{Z_1'}{Z_1}. \quad (29)$$

Note that the energy obtained in the grand canonical formalism (superscript ‘gca’) coincides with that obtained in the canonical formalism. Consequently, by equating that mean energy with m/n , the temperatures found will be the same in both formalisms. The same situation happens in the case of the heat capacity, so that:

$$T_{\text{osc}}^{\text{gca}} = T_{\text{osc}}^{\text{can}}, \quad (30)$$

$$T_{\text{two}}^{\text{gca}} = T_{\text{two}}^{\text{can}}, \quad (31)$$

$$C_{\text{osc}}^{\text{gca}} = C_{\text{osc}}^{\text{can}}, \quad (32)$$

$$C_{\text{two}}^{\text{gca}} = C_{\text{two}}^{\text{can}}. \quad (33)$$

To determine the chemical potential, remember that the number of particles in the grand canonical formalism is calculated as:

$$n = \left(\frac{\partial \ln \mathbf{Z}}{\partial \left(\frac{\mu}{T} \right)} \right)_T = \frac{e^{\mu/T} Z_1}{1 - e^{\mu/T} Z_1}. \quad (34)$$

From this, it follows that:

$$\mu^{\text{gca}} = -T \ln \left[\frac{(n+1)Z_1}{n} \right]. \quad (35)$$

Then, taking the expression for Z_{osc} given by (16) and taking into account (18) and (30), it follows that:

$$\mu_{\text{osc}}^{\text{gca}} = - \ln \left[\frac{n+m}{n+1} \right] / \ln \left[\frac{n+m}{m} \right]. \quad (36)$$

Similarly, for the two-level systems cluster: Z_{two} given by (22) is used, and (24) and (31) are taken into account. This gives:

$$\mu_{\text{two}}^{\text{gca}} = \ln \left[\frac{n-m}{n+1} \right] / \ln \left[\frac{n-m}{m} \right]. \quad (37)$$

Note that, since the volume and pressure are not defined for the analysed models, the entropy can be expressed generally as: $S = E/T - n \mu/T$. From the above expressions, it follows that:

$$S^{\text{gca}} = n T \frac{Z_1'}{Z_1} + n \ln Z_1 + n \ln \left[\frac{n+1}{n} \right]. \quad (38)$$

For the harmonic oscillator, this expression and equations (16), (18) and (30) give:

$$S_{\text{osc}}^{\text{gca}} = n \ln \left[\frac{n+m}{n} \right] + m \ln \left[\frac{n+m}{m} \right] + n \ln \left[\frac{n+1}{n} \right]. \quad (39)$$

Similarly, applying (22), (24) and (31)–(38) gives the entropy of the two-level systems cluster:

$$S_{\text{two}}^{\text{gca}} = n \ln \left[\frac{n}{n-m} \right] - m \ln \left[\frac{m}{n-m} \right] + n \ln \left[\frac{n+1}{n} \right]. \quad (40)$$

Thus, the calculations proposed at the beginning of the article are completed. Some thermodynamic properties (T , μ , S , C) have been expressed in terms of the fundamental constituents of the system: the number of particles n and the number of energy quanta m , following the microcanonical, canonical and grand canonical formalisms.

5. Analysis and discussion

For easy viewing, results for the harmonic oscillator are shown in table 1, while those for the two-level systems cluster appear in table 2.

5.1. The three formalisms yield different results for very small systems ($n \sim 10$)

Figure 1(a) shows the entropy for a cluster of oscillators (figure 2(a) for the two-level systems) with $n = 10$ in relation to the number of energy quanta m . Clearly, with such a small system the results differ significantly according to the formalism used. This can also be said for the heat capacity, which is shown in figures 1(c) and 2(c).

Table 1. Thermodynamic properties of a cluster with n harmonic oscillators and m energy quanta evaluated within the microcanonical, canonical and grand canonical formalisms.

	Microcanonical	Canonical	Grand canonical
T	$1 / \ln \left[\frac{n+m-1}{m} \right]$	$1 / \ln \left[\frac{n+m}{m} \right]$	$1 / \ln \left[\frac{n+m}{m} \right]$
μ	$-\ln \left[\frac{m+n-1}{n-1} \right] / \ln \left[\frac{m+n-1}{m} \right]$	$-\ln \left[\frac{m+n}{n} \right] / \ln \left[\frac{m+n}{m} \right]$	$-\ln \left[\frac{n+m}{n+1} \right] / \ln \left[\frac{n+m}{m} \right]$
S	$\sum_{k=1}^m \ln \left[\frac{k+n-1}{k} \right]$	$n \ln \left[\frac{n+m}{n} \right] + m \ln \left[\frac{n+m}{m} \right]$	$n \ln \left[\frac{n+m}{n} \right] + m \ln \left[\frac{n+m}{m} \right] + n \ln \left[\frac{n+1}{n} \right]$
C	$\frac{\ln \left[\frac{m+n}{1+m} \right] \ln \left[\frac{m+n-1}{m} \right]}{\ln \left[\frac{(n+m-1)(m+1)}{m(n+m)} \right]}$	$\frac{m}{n}(m+n) \left(\ln \left[\frac{n+m}{m} \right] \right)^2$	$\frac{m}{n}(m+n) \left(\ln \left[\frac{n+m}{m} \right] \right)^2$

 ∞

Table 2. Thermodynamic properties of a cluster with n two-level systems with and m energy quanta evaluated within the usual formalisms.

	Microcanonical	Canonical	Grand canonical
T	$1 / \ln \left[\frac{n-m+1}{m} \right]$	$1 / \ln \left[\frac{n-m}{m} \right]$	$1 / \ln \left[\frac{n-m}{m} \right]$
μ	$\ln \left[\frac{n-m}{n} \right] / \ln \left[\frac{n-m+1}{m} \right]$	$\ln \left[\frac{n-m}{n} \right] / \ln \left[\frac{n-m}{m} \right]$	$\ln \left[\frac{n-m}{n+1} \right] / \ln \left[\frac{n-m}{m} \right]$
S	$\sum_{k=1}^{n-m} \ln \left[\frac{k+m}{k} \right]$	$n \ln \left[\frac{n}{n-m} \right] - m \ln \left[\frac{m}{n-m} \right]$	$n \ln \left[\frac{n}{n-m} \right] - m \ln \left[\frac{m}{n-m} \right] + n \ln \left[\frac{n+1}{n} \right]$
C	$\frac{\ln \left[\frac{n-m+1}{m} \right] \ln \left[\frac{n-m}{m+1} \right]}{\ln \left[\frac{(n-m+1)(m+1)}{m(n-m)} \right]}$	$\frac{m}{n} (n-m) \left(\ln \left[\frac{n-m}{m} \right] \right)^2$	$\frac{m}{n} (n-m) \left(\ln \left[\frac{n-m}{m} \right] \right)^2$

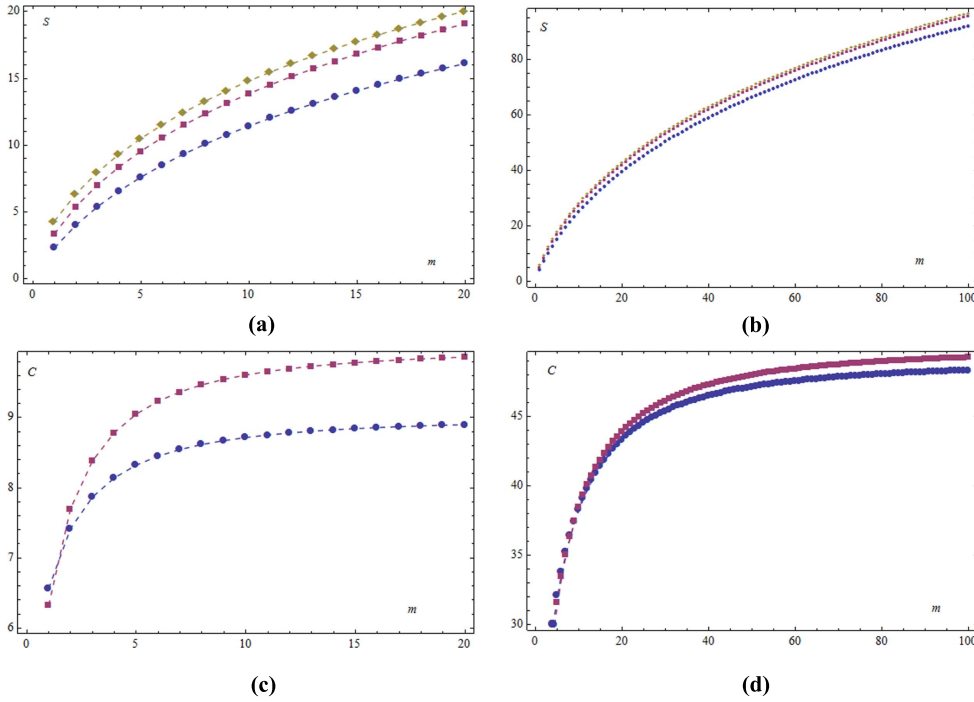


Figure 1. Thermodynamic properties for a cluster of n quantum oscillators in terms of the energy quanta m present in the system. The entropy S is considered for two different sizes in (a) $n = 10$ and (b) $n = 50$. And the heat capacity C is seen in (c) $n = 10$ and (d) $n = 50$. Calculations have been made using the microcanonical (\bullet), canonical (\blacksquare) and grand canonical (\blacklozenge) formalisms. The text explains that C evaluated within the grand canonical ensemble coincides with that from the canonical ensemble; for that reason, only two curves appear in (c) and (d): the upper curve corresponds to the canonical formalism and the lower curve to the microcanonical one. Note that, in the canonical formalism, the heat capacity *per oscillator* tends to 1 for both $n = 10$ and $n = 50$, which is the behaviour observed in the thermodynamic limit. This does not occur in the microcanonical ensemble, and the difference, at least for $n = 10$, would be observable experimentally.

With such small sizes, the difference between the results found in the canonical or microcanonical formalism would be experimentally detectable. For this, the cluster of quantum oscillators must be related to the Einstein solid [2–4], keeping in mind that such model is based on the assumption that a solid with n atoms can be thought of as a set of $3n$ quantum oscillators. Let us call N_A the Avogadro constant; if one mole is considered, i.e. N_A atoms, it is easy to demonstrate that the heat capacity reaches a limit value equal to $3k_B N_A$, independently of the formalism used. Considering that this article works with such units that $k_B = 1$, then the heat capacity *per oscillator* tends to the limit value 1 in the thermodynamic limit. From figures 1(c) (10 oscillators) and (d) (50 oscillators), it can be concluded that the heat capacity *per oscillator* tends to the value 1 within the canonical formalism but *not* within the microcanonical formalism. That is to say that the calculations using the canonical ensemble behave as is expected in the thermodynamic limit, even when working with really small systems (10–50 particles). When the microcanonical ensemble is used, the limit value for the heat capacity depends on the size of the system, as expected. In the case of a

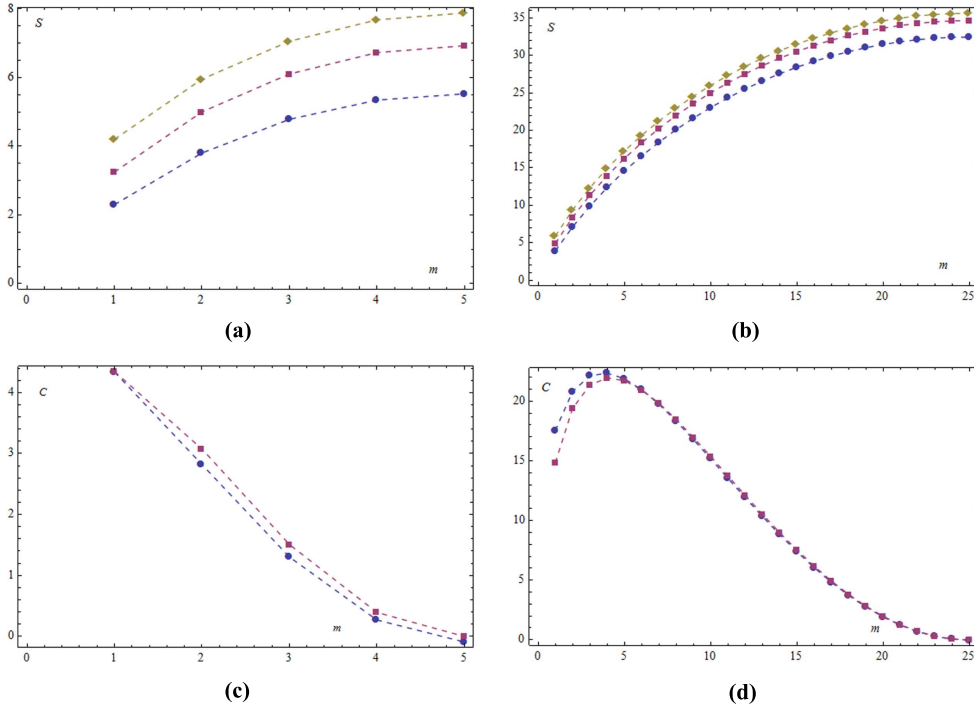


Figure 2. Thermodynamic properties for a cluster of n two-level systems in terms of the energy quanta m present in the system. The entropy S is considered for two different sizes in (a) $n = 10$ and (b) $n = 50$. And the heat capacity C is seen in (c) $n = 10$ and (d) $n = 50$. Calculations have been made using the microcanonical (●), canonical (■) and grand canonical (◆) formalism. The text explains that C evaluated within the grand canonical ensemble coincides with that from the canonical ensemble.

10-particle system, the difference with the canonical result is of the order of 10%, which is therefore experimentally verifiable.

A comment on the relations of the canonical and grand canonical formalisms is due. The entropy is greater in the grand canonical ensemble than in the canonical one as can be seen from (38) although the temperature is the same—equation (30). This can be intuitively understood: a system in the grand canonical ensemble can exchange energy *and particles* with the reservoir while the same system in the canonical formalism can only exchange energy. Thus there are more accessible microstates to the system in the first case and, consequently, the entropy is greater. Notice—see figures 1(a) and 2(a)—that the microcanonical entropy is even lower than the canonical one: the system does not interchange energy and less microstates are accessible. One can say that as the system is more open, the number of accessible microstates increases and the entropy is greater.

Regarding the chemical potential, there is no simple explanation why it is different in the three formalisms. As Callen [10] has pointed out, we do not have an intuitive understanding of the chemical potential as we have of the temperature or the pressure. For this reason the chemical potential receives little attention in physics teaching [11]. Nevertheless it is interesting to remark a recent result [12]. If the zero-point energy of the oscillators is taken into account, it is found that $\mu(T) = 0$ for $T < T^*$ where T^* depends on the size of the system

($T^* \rightarrow 0$ as $N \rightarrow \infty$). This fact might be a sign of a sort of Bose-Einstein condensation in a finite-size system but the question deserves further discussion among researchers¹.

5.2. Equivalence of the ensembles in the thermodynamic limit

The temperature and chemical potential evaluated within the three ensembles are clearly equivalent in the thermodynamic limit. It would suffice to compare the elements in the first two rows of tables 1 and 2 to verify that the difference between them is a term of order $+/-1$ that is irrelevant when n is large.

The equivalence of the entropy and heat capacity within the canonical and grand canonical ensembles is also clear. The formulas for the heat capacity are the same in both ensembles and, according to (38), the entropy is: $S^{\text{gca}} = S^{\text{ca}} + n \ln [1 + 1/n]$; therefore, for a large number of particles, they both coincide.

An equivalence between the formulas for the entropy and heat capacity obtained with the microcanonical and canonical ensembles is not readily evident, but can be inferred from figures 1(b), (d), 2(b) and (d) showing the entropy and heat capacity for clusters with $n = 50$ elements. It can be observed that the difference between the results from the two ensembles is much smaller than in the case of $n = 10$. If the calculations are repeated with a few hundred particles, the curves become indistinguishable.

5.3. Non-additivity of the entropy

A non-obvious issue is whether the additivity of the entropy, which is a basic axiom of thermodynamics [10], is satisfied for such small systems. To test this, the relative difference is quantified for a larger system, with n particles and m energy quanta, against two smaller systems, with half the particles and quanta. A property ΔS_{rel} is thus defined, given by:

$$\Delta S_{\text{rel}}(n, m) = \frac{\left[S(n, m) - 2S\left(\frac{n}{2}, \frac{m}{2}\right) \right]}{S(n, m)} * 100. \quad (41)$$

In the case of the oscillators, within the canonical formalism the difference is strictly zero, as can be easily seen from (20):

$$\Delta S_{\text{rel}_{\text{osc}}^{\text{can}}} = 0. \quad (42)$$

Through the microcanonical formalism, an analytical formula for the entropy difference can be found, but it lacks usefulness since it is complicated and makes use of special functions. It is more useful to evaluate the difference (41) numerically. The result can be seen in figure 3(a) (upper curve) where ΔS_{rel} is shown in terms of the system size for the case where $m = n$. It can be observed that the difference is higher than 10% for a system with 10 particles and drops to $\sim 2\%$ for $n = 100$.

Regarding the grand canonical ensemble, it can be demonstrated from (39) that:

$$\left[S_{\text{osc}^{\text{gca}}}(n, m) - 2S_{\text{osc}^{\text{gca}}}\left(\frac{n}{2}, \frac{m}{2}\right) \right] \rightarrow -1 \text{ if } n \rightarrow \infty. \quad (43)$$

¹ In [12] a discrete version of the Leibniz integration rule is used to deal with a small number of particles, but the approach used in this paper—replacing derivatives by finite differences—is straightforward and intuitive. A finite difference scheme for a few-particle system represents what actually happens: a particle or quanta is added to the system and one evaluates the change in a thermodynamic magnitude.

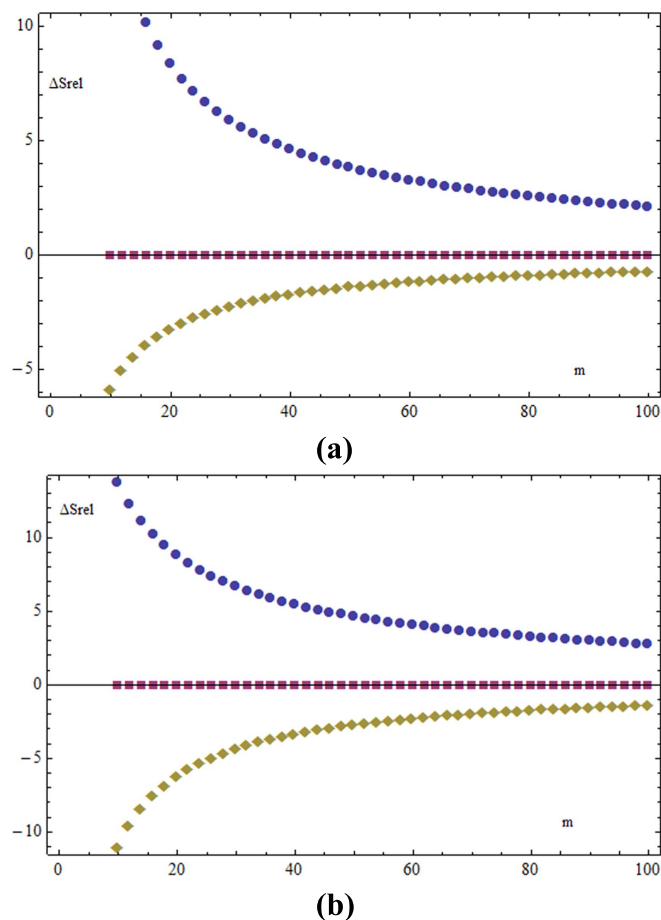


Figure 3. Non-additivity of the entropy for small systems. This figure shows the relative difference ΔS_{rel} between the entropy of a system with n particles and m quanta and that of two systems with half the elements—see equation (41)—in terms of the size of the system. Calculations follow the microcanonical (●), canonical (■) and grand canonical (◆) formalism. For oscillators (a) the case when $m = n$ is shown. For two-level systems (b) the case $m = n/2$ is plotted. Note that the entropy cannot be said to be additive for $n = 10$, i.e., a fundamental assumption of thermodynamics is not verified; only when the system has a few hundred elements, such an assumption can be considered valid. It should be highlighted that the canonical formalism does *not* detect this characteristic of small systems.

Therefore, $\Delta S_{rel_{osc}}^{gca} \rightarrow 0$ in the thermodynamic limit, as expected. Its behaviour for small sizes is shown in figure 3(a) (lower curve): for $n = 10$ the difference is $\sim 6\%$ and it drops rapidly to 1% for $n = 100$.

In the case of the two-level systems cluster, the results are similar to those of the oscillator. It becomes immediately clear from (26) and (41) that, within the canonical ensemble, the relative entropy difference is identically zero for all n and m :

$$\Delta S_{rel_{two}}^{can} = 0. \quad (44)$$

Within the microcanonical ensemble, an analytical formula can be found for equation (41), but it is not very useful since it is expressed in terms of the generalised zeta function. It is more convenient to plot $\Delta S_{\text{rel}_{\text{two}}^{\text{mic}}}$ as shown in figure 3(b) (upper curve). It can be seen that the relative entropy difference is of the order of 14% for $n = 10$ and $m = n/2$, and it drops to 3% for a system with 100 particles. Within the grand canonical ensemble (lower curve of figure 3(b)), the difference decreases rapidly and is lower than 2% for systems with 100 elements.

In conclusion, it is clear that a fundamental assumption of thermodynamics holds valid for systems with a few hundred particles, but not so for systems with $n < 10^2$.

A critical remark should be made here about the canonical formalism. It is undoubtedly the most used, but perhaps it may oversimplify reality: both the microcanonical and grand canonical ensembles show that the entropy is non-additive for small systems, whereas the canonical ensemble does not even detect this characteristic.

5.4. Canonical or microcanonical ensemble?

In this work, certain thermodynamic properties have been expressed in terms of the number of particles and the number of energy quanta, i.e., the natural variables of the microcanonical ensemble. The reason for this choice is that particles and energy quanta are the fundamental constituents in nature; temperature, being a derived property, has not been assigned a central value. However, to make comparisons with experimental results, it is easier to control the temperature than the number of energy quanta. For this, m must be expressed as a function of T from (18) for the oscillators and from (24) for the two-level systems. By replacing m , the different thermodynamic properties are found as a function of T .

For the oscillators cluster, the following expressions give the heat capacity:

$$C_{\text{osc}}^{\text{mic}} = \frac{\ln[ne^{1/T} - 1] - \ln[e^{1/T} + n - 2]}{1 + T \ln[e^{1/T} + n - 2] - T \ln[ne^{1/T} - 1]}, \quad (45)$$

$$C_{\text{osc}}^{\text{can}} = \frac{n}{T^2} \frac{e^{1/T}}{(e^{1/T} - 1)^2}. \quad (46)$$

Figure 4(a) shows the heat capacity in terms of the temperature for a cluster of oscillators evaluated within both the canonical and microcanonical ensembles. As mentioned above, the limit value of the heat capacity in the case of the oscillators should be kept in mind. When the canonical ensemble is used, the heat capacity *per oscillator* tends to 1, as in the thermodynamic limit. However, in the microcanonical ensemble, the limit value is lower. That difference is a quantitative measure of the difference between both formalisms and it would be experimentally verifiable. From (45), it follows that when $T \rightarrow \infty$, $C_{\text{osc}}^{\text{mic}} \rightarrow (n - 1)$. Therefore, the heat capacity *per oscillator* goes to $(1 - 1/n)k_B$ when normal units are used. For a system with $n = 10$, the difference reaches 10%, which is detectable with the current accuracy levels for measuring heat capacities.

For the two-level systems cluster, the expressions for the heat capacity as a function of temperature are:

$$C_{\text{two}}^{\text{mic}} = \frac{\ln[e^{1/T}n - 1] - \ln[e^{1/T} + n + 2]}{1 + T \ln[e^{1/T} + n + 2] - T \ln[e^{1/T}n - 1]}, \quad (47)$$

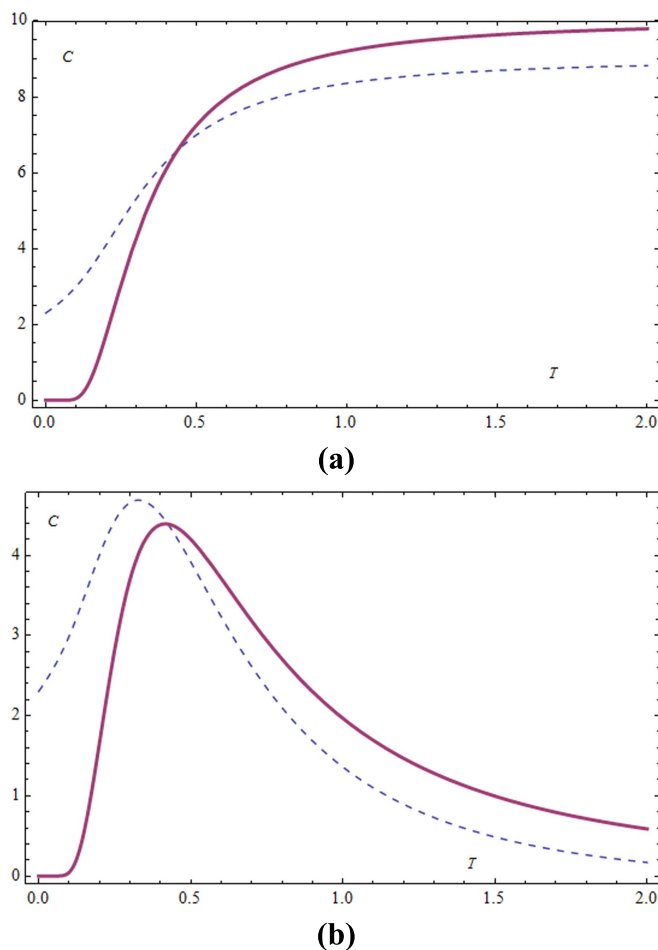


Figure 4. Heat capacity as a function of temperature for a cluster of $n = 10$ elements. (a) shows the case of harmonic oscillators and (b) two-level systems. The heat capacity has been evaluated within the canonical (solid line) and microcanonical (dashed line) formalism. For this size, the difference between both ensembles is relevant. Note that for the oscillators, the canonical heat capacity per oscillator tends to 1, as in the thermodynamic limit, while the limit value of the microcanonical heat capacity is 0.9. This difference falls within what can be measured experimentally and, therefore, it would allow deciding which of the two formalisms is more appropriate for such small sizes.

$$C_{\text{two}}^{\text{can}} = \frac{n}{T^2}(e^{1/2T} + e^{-1/2T})^{-2}. \quad (48)$$

These expressions are plotted in figure 4(b) for $n = 10$. It can be observed that there is a significant difference between both curves, which might be detected experimentally.

A remark on the different formalisms of statistical mechanics is due. The microcanonical formalism assumes that the system is isolated, thus E is constant while the canonical one supposes the system is in contact with a heat reservoir at a given T and the energy fluctuates, however the average energy \bar{E} is constant. It is shown that $E = \bar{E}$ in the thermodynamics limit, and the other thermal magnitudes take the same value regardless the applied formalism.

This means that those magnitudes, for example the heat capacity, are *independent of the system environment*. In section 3—equations (17) and (23)—it was clear to equate the average energy from the canonical formalism with m/n which are microcanonical variables. In this way the mentioned equivalence holds naturally. However heat capacities obtained with both formalisms are not equivalent for few-particle systems. Does it mean that the heat capacity of such small systems depends on the environment? From a formal point of view the answer is affirmative, though one should be cautious with purely mathematical results; experimentalists should finally decide the question.

As far as this author knows, experiments measuring the heat capacity of a few-particle system in different environments have not carried out yet, but semiconductor nanostructures seem to be suitable for performing them. In particular electrons trapped in a harmonic potential or a quantum well are good candidates. Of course, in this situation the fermionic properties of electrons should be taken into account [13–15].

6. Final remarks

The first point to highlight is the robustness of conventional statistical mechanics. For systems with hundreds of particles, the difference between the three ensembles is small, and for a few thousand particles, the results are totally indistinguishable. Thus, conventional wisdom can be said to be validated.

However, it is clear that for systems with $n < 10^2$ particles the three usual formalisms yield different results, and that such a difference could be detected experimentally. On this point, figure 4 may be the one deserving more attention in this article.

Regarding the use of the canonical formalism for such small systems, an interesting issue has been presented here. As stated above, the partition function of a particle Z_1 is calculated, and then the partition function of the total system is considered to be simply Z_1^n . In a sample with a few particles, this leads to properties such as the heat capacity or entropy per particle to behave as in the thermodynamic limit. However, the microcanonical ensemble shows that these properties depend on the number of particles; besides, that is what is observed in the experiments. Therefore, it would seem that the canonical ensemble cannot deal properly with systems with tens of elements, and the microcanonical one would appear to be more appropriate for this.

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