INEQUIVALENCE OF CANONICAL AND GRAND CANONICAL ENSEMBLES FOR BOSONIC SYSTEMS

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For many-particle quantum systems, calculating thermodynamic quantities in the canonical ensemble is a very hard task, while this is tractable in the grand canonical ensemble. The second ensemble is then used. The results are supposed to be the same, at least in the thermodynamic limit. Is this actually the case? In this work, we consider a system of N non-interacting bosons distributed among few energy levels. We can calculate the canonical partition function in this case and deduce the canonical mean energy. We compare it to the mean energy deduced from the grand canonical ensemble for the same number of particles. We consider the case of a large number of particles.

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1. Introduction

For many-particle quantum systems (bosons and fermions), calculating the canonical partition function is a very hard task. This is due to the indistinguishability of identical quantum particles. The use of canonical ensemble is then avoided. As the grand canonical partition function is more tractable, thermodynamic quantities are calculated using the grand canonical ensemble. The results are supposed to be the same, at least in the thermodynamic limit [1]. Is this actually the case? Furthermore, there is many systems with fixed number of particles, where the canonical description is more appropriate [2].

It is usually stated in textbooks that the different statistical ensembles are equivalent, at least in the thermodynamic limit [3, 4]. These ensembles are supposed to give the same thermodynamic quantities in this limit. But

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during the last two decades, this equivalence has been subject to a renewed interest. It has been shown first that the microcanonical and the grand canonical ensembles are not equivalent for the calculation of the ground state population in the Bose–Einstein condensate [5].

Later, the equivalence between the microcanonical and the canonical ensembles has been studied deeply [6–17]. In particular, it has been proved that these ensembles are equivalent only when the microcanonical entropy is a concave function of the energy. For systems of interacting spins, it has been shown that the equivalence is realized only for short range interactions.

In this work, we are interested in testing the equivalence of the canonical and grand canonical ensembles for systems of non-interacting bosons. For this aim, we compare the mean energy obtained in the canonical ensemble to that of the grand canonical one. We consider a system of bosons without interactions, distributed among few energy levels, that is a system with a bounded spectrum. For such systems, the equivalence between these ensembles cannot be taken for granted [18].

We can calculate the canonical partition function in this case and deduce the canonical mean energy. We compare it to the result obtained by use of the grand canonical ensemble in order to test the equivalence of the two ensembles.

For our calculations, we use the following notations: the subscript is for the ensemble (GC for grand canonical and C for canonical) and the superscript is for the levels number; for example, $Q_{\mathrm{C}}^{(n)}$ is the canonical partition function for a system of n energy levels and $Q_{\mathrm{GC}}^{(n)}$ the grand canonical partition function for n energy levels.

2. Two energy levels system

We consider a system where N identical spinless bosons without interaction are distributed among two energy levels. Without a loss of generality, we can take the energy values of these levels as 0 and ε respectively. The system is in thermal equilibrium with a heat bath of temperature T. We want to calculate the mean energy using the canonical and grand canonical ensembles and compare the obtained values.

2.1. Canonical ensemble

Generally, the calculation of the canonical partition function is difficult. We can evaluate it easily in this case. For this aim, we distribute N indistinguishable bosons among these two levels. We put i bosons on the level of energy ε and $(N-i)$ bosons on the level of energy 0. A distribution is

represented in figure 1. The energy of the system is $i\varepsilon$. We obtain all the possible configurations by varying i from 0 to N.

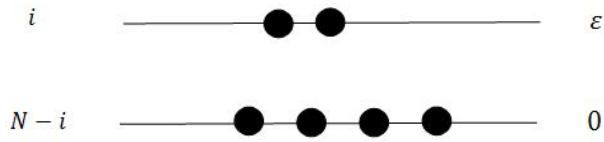

Fig. 1. A distribution of N indistinguishable bosons among two energy levels. The energy of this distribution is $i\varepsilon$.

Then, the canonical partition function can be written in the form [19]

$$Q_{\mathrm{C}}^{(2)} = \sum_{i=0}^{N} e^{-i\beta\varepsilon}\,, \tag{1}$$

where $\beta = 1/kT$, and k is the Boltzmann constant. This sum is a geometric series, with the result

$$Q_{\mathrm{C}}^{(2)} = \frac{1 - e^{-(N+1)\beta\varepsilon}}{1 - e^{-\beta\varepsilon}}\,. \tag{2}$$

The mean energy of the system is given by the relation

$$\bar{E}_{\mathrm{C}}^{(2)} = -\frac{\partial \mathrm{Log} Q_{\mathrm{C}}^{(2)}}{\partial\beta}\,. \tag{3}$$

It takes the form

$$\bar{E}_{\mathrm{C}}^{(2)} = \frac{\varepsilon}{e^{-\beta\varepsilon} - 1} - \frac{(N+1)\varepsilon}{e^{-(N+1)\beta\varepsilon} - 1}\,, \tag{4}$$

where $\bar{E}_{\mathrm{C}}^{(2)}/\varepsilon$ is a function of N and $\beta\varepsilon$. We notice that this energy is not additive; this is due to quantum correlations between bosons.

2.2. Grand canonical ensemble

For this system, the grand canonical partition function is [20]

$$Q_{\mathrm{GC}}^{(2)} = \frac{1}{(-1 + e^{\beta\varepsilon - \beta\mu})}\frac{1}{(-1 + e^{-\beta\mu})}\,, \tag{5}$$

where μ is the chemical potential. The mean number of particles is given by the relation

$$\bar{N}_{\mathrm{GC}}^{(2)} = \frac{1}{(-1 + e^{\beta\varepsilon - \beta\mu})} + \frac{1}{(-1 + e^{-\beta\mu})}\,. \tag{6}$$

This relation determines μ when $\bar{N}^{(2)}_{\rm GC}$ is fixed, for a given $\beta\varepsilon$. $\bar{N}^{(2)}_{\rm GC}$ is a function of $\beta\varepsilon$ and $\beta\mu$. The grand canonical mean energy has the form

$$\bar{E}^{(2)}_{\rm GC} = \frac{\varepsilon}{(-1 + e^{\beta\varepsilon - \beta\mu})}\,, \tag{7}$$

where $\bar{E}^{(2)}_{\rm GC}/\varepsilon$ is a function of $\beta\varepsilon$ and $\beta\mu$.

2.3. Comparison for fixed N

In this case, for a fixed N and for a value of $\beta\varepsilon$, we calculate $\bar{E}^{(2)}_{\rm C}$ (equation (4)). To compute the mean energy $\bar{E}^{(2)}_{\rm GC}$, we first determine the chemical potential μ which leads to the fixed number $\bar{N}^{(2)}_{\rm GC}$ (equation (6)) taken equal to N and then use this value to obtain $\bar{E}^{(2)}_{\rm GC}$. It is convenient to consider the relative discrepancy of the mean energy

$$R = \frac{\left| \bar{E}^{(2)}_{\rm GC} - \bar{E}^{(2)}_{\rm C} \right|}{\bar{E}^{(2)}_{\rm GC}}\,. \tag{8}$$

We have computed the relative discrepancy R as a function of $\beta\varepsilon$ for $N = 10^3$ and $N = 10^5$. The results are shown in figure 2. The curves have a Gaussian shape with a maximum of R equal to 21%. We notice that this maximum is the same for different values of N.

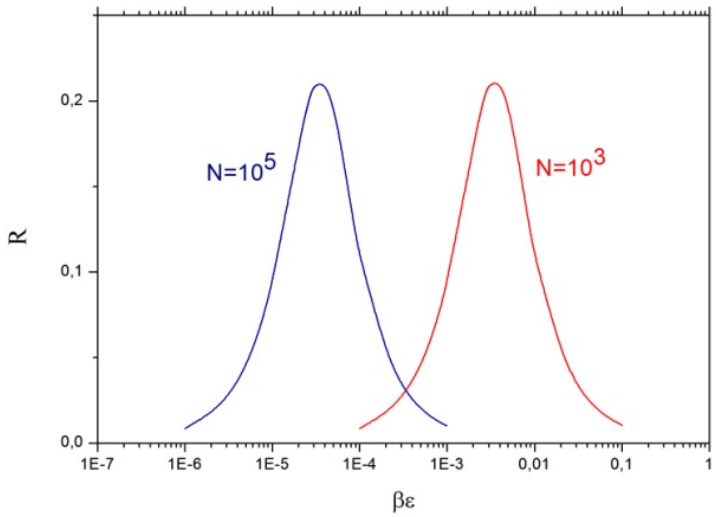

Fig. 2. (Colour on-line) The relative discrepancy R as a function of $\beta\varepsilon$ for a two levels system with a fixed value of N (indicated on the curve).

2.4. Comparison for a general case

We want to compare the canonical and grand canonical mean energies for systems of the same number of particles (at least on average) for different values of $\beta\varepsilon$ and $\beta\mu$. To realize this, we take the number N of particles in the canonical ensemble (equation (4)) equal to the average particles number of the grand canonical ensemble (equation (6))

$$N = \bar{N}^{(2)}_{\mathrm{GC}}(\beta\varepsilon, \beta\mu) \tag{9}$$

with this choice, $\bar{E}^{(2)}_{\mathrm{C}}/\varepsilon$ becomes a function of $\beta\varepsilon$ and $\beta\mu$

$$\frac{\bar{E}^{(2)}_{\mathrm{C}}}{\varepsilon} = \frac{1}{-1+e^{\beta\varepsilon}} - \frac{\bar{N}^{(2)}_{\mathrm{GC}}(\beta\varepsilon, \beta\mu)+1}{-1+e^{\left(\left(\bar{N}^{(2)}_{\mathrm{GC}}(\beta\varepsilon,\beta\epsilon)\right)+1\right)\beta\varepsilon}}\,. \tag{10}$$

The relative discrepancy R of these mean energies is then a function of $\beta\varepsilon$ and $\beta\mu$. We can write it in the form

$$R(\beta\varepsilon, \beta\mu) = \frac{\left|\, \bar{E}^{(2)}_{\mathrm{GC}}(\beta\varepsilon, \beta\mu) - \bar{E}^{(2)}_{\mathrm{C}}(\beta\varepsilon, \beta\mu) \,\right|}{\bar{E}^{(2)}_{\mathrm{GC}}(\beta\varepsilon, \beta\mu)}\,. \tag{11}$$

To understand the behaviour of $R(\beta\varepsilon, \beta\mu)$, we plot the contours of the same values of $R(\beta\varepsilon, \beta\mu)$ as a function of the two variables $\beta\varepsilon$ and $\beta\mu$. The result is shown in figure 3.

We see in figure 3 that the contours of constant values of $R(\beta\varepsilon, \beta\mu)$ are straight lines which pass by the origin. These lines are such that

$$\beta\varepsilon = -\lambda\beta\mu\,, \tag{12}$$

where λ is a positive parameter, which represents the slope of the line. It can be seen as the ratio of the energy gap ε on the chemical potential μ. We notice that the relative discrepancy is varying strongly with λ. So it is interesting to write R as a function of λ and $\beta\mu$ noted $R_p(\lambda, \beta\mu)$

$$R_p(\lambda, \beta\mu) = R(-\lambda\beta\mu, \beta\mu)\,. \tag{13}$$

When the slope of the line increases, the value of R increases and reaches a maximum (around 21%) and then decreases. The interesting case is the thermodynamic limit as it is stated in textbooks that the different statistical ensembles are equivalent in this limit [3, 4].

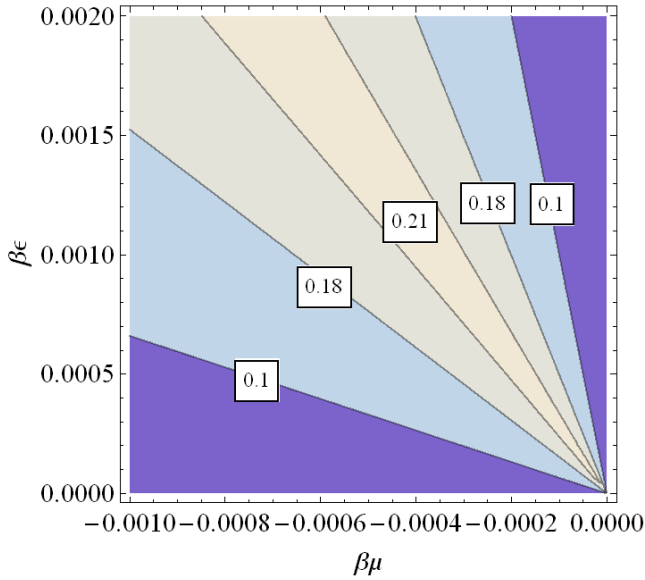

Fig. 3. (Colour on-line) Contours of constant values of $R(\beta\varepsilon, \beta\mu)$ as a function of $\beta\varepsilon$ and $\beta\mu$ for a two levels system. These contours are straight lines which pass by the origin. The values of $R(\beta\varepsilon, \beta\mu)$ are indicated on the corresponding lines. The value 21% concerns the lines of both sides.

For N particles in a box of volume V, this limit is written: $N \to \infty$, $V \to \infty$, and $\frac{N}{V}$ = constant. Taking $V \to \infty$ makes the level energy spacing ε' in the box go to zero. The constant particle density gives $N\varepsilon'^{3/2}$ constant for a box in three dimensions (3D case) and $N\varepsilon'$ constant for a two dimensional box (2D case).

In our system of two energy levels, the volume V is not involved, so we cannot consider a particle density and speak of a thermodynamic limit in a strict sense. However, we can define a "thermodynamic limit-like approach" when we take: $N \to \infty$, $\varepsilon \to 0$, and $N\varepsilon$ = constant. This looks like the thermodynamic limit in the 2D box case. This limit is obtained when $\beta\mu$ goes to zero. Then, equation (12) gives $\beta\epsilon \to 0$ and equation (6) ensures that $N\varepsilon$ is constant. In this "thermodynamic limit-like approach", the relative discrepancy of the mean energy depends only on λ

$$R_{\text{th}}(\lambda) = \lim_{\beta\mu \to\, 0} R_p(\lambda, \beta\mu)\,. \tag{14}$$

For a system of two energy levels, the expression of $R_{\text{th}}(\lambda)$ is

$$R_{\text{th}}(\lambda) = \frac{1}{\lambda} - \frac{\lambda + 2}{e^{\lambda(\lambda+2)(\lambda+1)} - 1}\,. \tag{15}$$

We plot $R_{\text{th}}(\lambda)$ as a function of λ. The result is shown in figure 4.

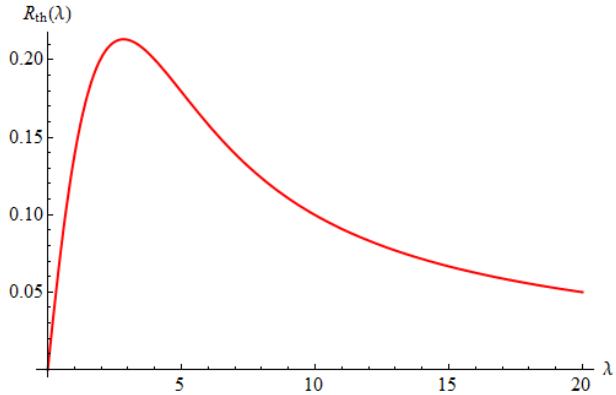

Fig. 4. Relative discrepancy $R_{\text{th}}(\lambda)$ in the "thermodynamic limit-like approach" as a function of λ for a two levels system.

From figure 4, we see that the relative discrepancy is not vanishing. It takes a maximum value of 21% for a value of λ around 2. It diminishes slowly towards zero when λ increases. We can conclude that, for a system with two energy levels, the canonical and grand canonical ensembles are not equivalent for the mean energy even in the "thermodynamic limit-like approach".

3. Three and more energy levels systems

We consider a system of N ideal spinless bosons distributed among three energy levels, equally spaced. The energy values are taken as 0, ϵ, 2ϵ, respectively. We show in figure 5 a distribution of particles among these levels.

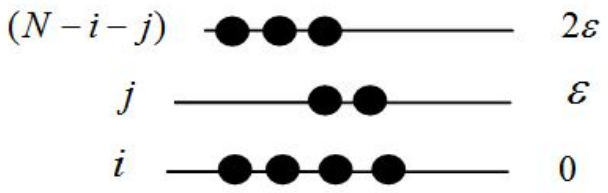

Fig. 5. Simple representation of a system with N ideal bosons distributed among three equidistant energy levels.

3.1. Canonical ensemble

A particle distribution is, for example, i bosons in the ground state (0), j bosons in the first state (ϵ), and $(N-i-j)$ in the second excited state (2ϵ).

To describe all reachable states to the system, we sum over i varying from 0 to N and, for a given i, we sum over j varying from 0 to $(N-i)$. The canonical partition function can be written then as

$$Q_{\mathrm{C}}^{(3)} = \sum_{i=0}^{N} \sum_{j=0}^{N-i} e^{-(0\times i+\beta\varepsilon\times j+2\beta\epsilon\times(N-i-j))} . \tag{16}$$

This gives the result

$$Q_{\mathrm{C}}^{(3)} = \frac{1-e^{-\beta\varepsilon(N+1)}}{1-e^{-\beta\varepsilon}} \times \frac{1-e^{-\beta\varepsilon(N+2)}}{1-e^{-2\beta\varepsilon}} . \tag{17}$$

The mean energy takes the form

$$\bar{E}_{\mathrm{C}}^{(3)} = \frac{\varepsilon}{(-1+e^{\beta\varepsilon})} - \frac{(N+1)\varepsilon}{-1+e^{(N+1)\beta\varepsilon}} + \frac{2\varepsilon}{(-1+e^{2\beta\varepsilon})} - \frac{(N+2)\varepsilon}{-1+e^{(N+2)\beta\varepsilon}} , \tag{18}$$

where $\bar{E}_{\mathrm{C}}^{(3)}/\varepsilon$ is a function of N and $\beta\varepsilon$.

3.2. Grand canonical ensemble

For this system, the grand canonical partition function is

$$\bar{Q}_{\mathrm{GC}}^{(3)} = \frac{1}{(1-e^{\beta\mu})} \frac{1}{(1-e^{\beta\mu-\beta\epsilon})} \frac{1}{1-e^{\beta\mu-2\beta\varepsilon})} . \tag{19}$$

The chemical potential μ is related to the mean particle number by the relation

$$\bar{N}_{\mathrm{GC}}^{(3)} = \frac{1}{-1+e^{-\beta\mu}} + \frac{1}{-1+e^{\beta\epsilon-\beta\mu}} + \frac{1}{-1+e^{2\beta\varepsilon-\beta\mu}} . \tag{20}$$

The mean energy has the form

$$\bar{E}_{\mathrm{GC}}^{(3)} = \frac{\varepsilon}{(-1+e^{\beta\varepsilon-\beta\mu})} + \frac{2\varepsilon}{-1+e^{2\beta\varepsilon-\beta\mu}} . \tag{21}$$

In order to compare the canonical and grand canonical mean energies, we follow the same procedure as done for the two levels system: we take the number of particles in the canonical ensemble equal to the average number of

particles in the grand canonical ensemble. We plot the relative discrepancy as a function of $\beta\epsilon$ and $\beta\mu$. As for the previous case, the contours of constant relative discrepancy are also straight lines passing by the origin. We impose also a linear relationship between $\beta\epsilon$ and $\beta\mu$ (equation (12)). We calculate the relative discrepancy in our "thermodynamic limit-like approach".

We develop similar calculations for systems with four and ten equidistant energy levels.

In figure 6, we present the relative discrepancy derived from the two ensembles in the "thermodynamic limit-like approach".

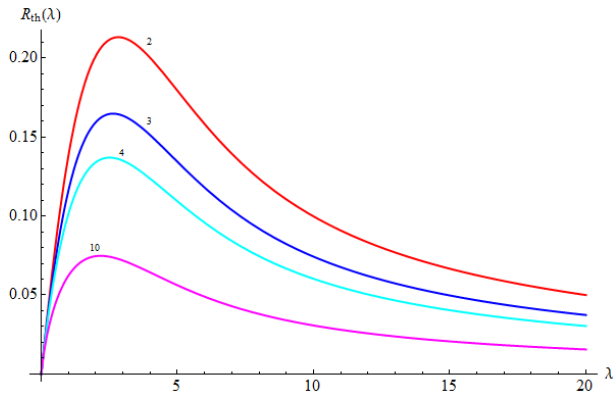

Fig. 6. (Colour on-line) Relative discrepancy $R_{\rm th}(\lambda)$ in the "thermodynamic limit-like approach" as a function of λ for a system with two, three, four and ten levels. The curves are labelled by the numbers of energy levels. The maximum value of $R_{\rm th}(\lambda)$ diminishes when the level number increases.

4. Summary and discussion

We have considered systems of N non-interacting spinless bosons distributed among a small number of energy levels. We have determined the mean energy in the canonical ensemble and in the grand canonical one. We have calculated the relative discrepancy in a "thermodynamic limit-like approach" we have defined. This relative discrepancy proved to be non-zero and can reach 21% for a two levels system. We have considered also systems with 3, 4 and 10 levels. The relative discrepancy is not zero but its maximum decreases as the number of levels increases. It is 7% for a system of 10 equidistant energy levels.

We conclude that these two ensembles are not equivalent for systems with a small number of energy levels (systems with a bounded spectrum).

In view of the regular decrease of the relative discrepancy as the number of levels increases, we can expect that this discrepancy will be null when the number of levels is infinite. Therefore, the equivalence between these two ensembles will be effective for systems with an infinite number of levels (this is the case for bosons in a box and for bosons trapped in a harmonic potential). This is then in agreement with the statement in textbooks.

Until now, we do not know experimental work to study the equivalence of canonical and grand canonical ensembles. We believe that a system of bosonic atoms interacting with magnetic field (the Zeeman effect) can be used for this purpose.

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