# Bose-Einstein condensation in the canonical ensemble

**D K Sunko†**
Department of Physics,
Faculty of Science,
University of Zagreb,
Bijenička cesta 32,
HR-10000 Zagreb, Croatia.

**Abstract.** A simple description of Bose-Einstein condensation for non-interacting bosons is provided, based on an easily derived quantum correction to the canonical partition function. It is distinguished by the explicit appearance of the factor $N!$, which enhances the classical probability for finding bosons in the same state, and an elementary demonstration, that the transition should be sharper in temperature, as the number of particles in the system increases. The reasoning is made explicit for the usual example of the ideal-gas dispersion.

PACS numbers: 03.75.Fi, 05.70.Ce

## 1. Introduction

The classic textbook exposition of Bose-Einstein condensation is in terms of the grand canonical ensemble [1, 2]. The practical advantages of such an approach need no elaboration. There may, however, be several pedagogical disadvantages.

First, there appears a clean break between the canonical and grand canonical formalisms, as one moves from distinguishable (classical) to indistinguishable (quantum) particles. Second, beginners seem to have some psychological difficulties with the notion of a chemical potential [3]. Finally, the need to account for the lowest-energy single-particle state separately, when passing from the sum over states to an integral, may leave some lingering suspicion: did we put this in by hand?

The present article shows one way a teacher may try to overcome such obstacles. The canonical approach, once understood on the example of the classical ideal gas, can be carried over to describe Bose-Einstein condensation. The grand-canonical explanation can then take place in a setting already made familiar, the main result being expected.

† email: dks@phy.hr

In addition to these pedagogical considerations, there has been a recent renewal of interest in the canonical description of Bose-Einstein condensation [4], following its observation in small assemblies, of several thousand atoms.

Needless to say, the reader should not expect great originality in the factual content of this article. After all, the 'right' way to treat the Bose gas in the canonical ensemble is by explicit use of the virial expansion, as done, for example, in the textbook by Pathria [5]. However, the present article is not concerned with re-deriving textbook results in yet another way. Rather, the interest is in developing physical insight by way of a qualitative argument, grounded in what students know of the classical ideal gas. To this end, even the transition temperature is conveniently defined as the one where the classical partition function becomes negligible, rather than by the appearance of a condensate. The quantitative difference is slight, but physically revealing, as shown in section 4.

## 2. The requisites

There are several things the students are expected to know. First, that the classical canonical partition function for $N$ non-interacting particles may be written

$$Z_{C,\mathrm{class}}(N,\beta) = \frac{1}{N!}\left(\sum_{i=1}^{L} e^{-\beta\varepsilon_i}\right)^N , \tag{1}$$

where $L$ is the number of single-particle states. Second, that the grand canonical partition function for non-interacting bosons is

$$Z_G(\mu,\beta) = \prod_{i=1}^{L}\left(1 - e^{\beta(\mu-\varepsilon_i)}\right)^{-1} . \tag{2}$$

Third, that the general connection between the canonical and grand canonical partition functions is

$$Z_G(\mu,\beta) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_C(N,\beta). \tag{3}$$

As usual, the ensemble is imagined like a lottery: as long as the system is sampled at times separated by more than the thermalization time, each sample corresponds to drawing a configuration at random, from all possible ones.

## 3. The demonstration

### *3.1. The case of two bosons*

The canonical partition function for two bosons is written by inspection:

$$Z_C(2,\beta) = \sum_{1\le i\le j\le L} e^{-\beta(\varepsilon_i+\varepsilon_j)} = \frac{1}{2}\left[\left(\sum_{i=1}^{L} e^{-\beta\varepsilon_i}\right)^2 + \sum_{i=1}^{L} e^{-2\beta\varepsilon_i}\right]. \tag{4}$$

The key step is the second equality, which rewrites the restricted sum in terms of unrestricted ones. The ensuing first term is recognized as the classical partition function

(1), with the 'good Boltzmann counting' factor 1/2! in place, of course. The important point to make here is that correct accounting for indistinguishability is not limited to this factor, but also produces the second term above. Its effect is manifestly to enhance the probability to encounter configurations with both bosons in the same state. It *doubles* this probability, with respect to the prediction of the first (classical) term.

### *3.2. The case of N bosons*

When the above derivation is generalized to $N$ bosons, it becomes apparent that the enhancement by a factor of two, encountered above, is by $N!$, in general. This can be argued in two steps. First, one can always write the canonical partition function, according to the pattern above:

$$Z_C(N,\beta) = \frac{1}{N!}\left(\sum_{i=1}^{L} e^{-\beta\varepsilon_i}\right)^N + \{\ldots \text{quantum corrections} \ldots\}. \tag{5}$$

Next, and this is the crucial step, one can use the known form of the grand partition function,

$$Z_G(\mu,\beta) = \prod_{i=1}^{L}\left(1 + e^{\beta\mu}e^{-\beta\varepsilon_i} + \ldots + e^{\beta\mu N}e^{-N\beta\varepsilon_i} + \ldots\right), \tag{6}$$

to extract the *full* contribution of configurations, with all bosons in the same state, to the canonical partition function. This is done at length, as follows: we are looking for some of the terms which multiply $e^{\beta\mu N}$ when the above product is expanded; all of them together constitute the exact canonical partition function. Those we are trying to find, of the form $e^{-N\beta\varepsilon_i}$, where all $N$ bosons occupy the same single-particle state, are actually the easiest to extract, because they appear right next to a factor $e^{\beta\mu N}$, as explicitly written in the expression (6) above. The only way they can still appear next to an $e^{\beta\mu N}$, when the product is expanded, is to pick an $e^{\beta\mu N}e^{-N\beta\varepsilon_i}$ from a single factor in the product, and multiply it by a '1' from all the other factors. This can be done in $L$ ways, corresponding to which factor is chosen, $1 \le i \le L$. The conclusion is, that the *same* canonical partition function (5) can also be written in the form

$$Z_C(N,\beta) = \sum_{i=1}^{L} e^{-N\beta\varepsilon_i} + \{\ldots \text{terms with at least two occupied states} \ldots\}. \tag{7}$$

In other words, the correct weight of each term $e^{-N\beta\varepsilon_i}$ in the $N$-boson canonical partition function is *unity*, and not $1/N!$, as in the classical expression (1). This is the relative factor of $N!$, mentioned at the beginning.

Finally, the two expressions (5) and (7) can be combined, to yield

$$Z_C(N,\beta) = \frac{1}{N!}\left(\sum_{i=1}^{L} e^{-\beta\varepsilon_i}\right)^N + \left(1 - \frac{1}{N!}\right)\sum_{i=1}^{L} e^{-N\beta\varepsilon_i} + \{\ldots \text{other terms} \ldots\}. \tag{8}$$

The negligible correction $-1/N!$ recognizes, that one term of this type is already present in the classical part; it may be pedagogically reassuring to belabor such details.

### *3.3. Bose-Einstein condensation*

To obtain Bose-Einstein condensation, one must ask, is the enhancement by $N!$ a large or small one, considering the total number of configurations. The experimental situation is, if one plays the ensemble lottery above a certain temperature, one draws only 'normal' members. Below it, the probability suddenly becomes overwhelming, that a 'condensed' member will be drawn. To understand this, consider the number of terms in the two sums in the expression (8). The first has $L^N/N! \sim (L/N)^N$ terms; the second, $L$ terms. The key step here is to realize, that the *effective* number of states goes down with the temperature, $L \to L_{\text{eff}}(T)$, because states of higher energy become inaccessible. Hence, the two sums will have a roughly equal number of terms when†

$$\left(\frac{L_{\text{eff}}(T)}{N}\right)^N \sim L_{\text{eff}}(T). \tag{9}$$

Now, the ratio on the left is taken to the $N$-th power, with $N \sim 10^{23}$. Obviously, as soon as $L_{\text{eff}}(T)$ dips below $N$, this power will change value drastically, from 'infinity' to 'zero'. Hence, the probability to draw a member of the ensemble from the 'normal' collection of configurations will go to zero, all the more suddenly with temperature, the larger the number of particles.

## 4. Example

For the free-particle dispersion, the one-particle partition function reads

$$Z_C(1,\beta) = \frac{V}{\lambda_T^3}, \tag{10}$$

where $\lambda_T = h/\sqrt{2\pi mkT}$, the thermal de Broglie wavelength. The expression (8) may be written, in this case,

$$Z_C(N,\beta) = \left[\frac{e(V/N)}{\lambda_T^3}\right]^N + \frac{1}{\sqrt{N}}\left[\frac{(V/N)}{\lambda_T^3}\right] + \ldots, \tag{11}$$

with $N! \to (N/e)^N$, and it has been recognized, that the second term in equation (8) is simply $Z_C(1, N\beta)$. By the above arguments, the classically dominant configurations should become unobservable at a temperature $T'$, defined by

$$eV/N = \lambda_{T'}^3. \tag{12}$$

This differs from the usual (London's) estimate of $T_c$ by the appearance of $e = 2.71\ldots$, instead of $2.61\ldots$, the value of London's function $F(1) = \sum_m m^{-3/2}$. The reason for the discrepancy is that $T_c$ is defined differently, as the temperature at which a macroscopic condensate begins to appear. In effect, the criterion (12) shows, that the classical partition function still contributes to the free energy at temperatures slightly below $T_c$. Numerically, $T'$ is about 2.5% lower than $T_c$.

† The two appearances of $L_{\text{eff}}(T)$ in this estimate do not necessarily refer to the same function, but the qualitative argument does not depend on this.

A qualitative discussion of the neglected terms is now possible. Note that the classical term is 'geometrically' enhanced, or suppressed, by a power of $N$, while the fully condensed term only carries an 'arithmetical' factor $N^{-1/2}$. The omitted ones will have exponents in between: less than $N$, but greater than unity. Thus they are expected to be negligible with respect to the classical term above the critical temperature. Below it, when the ratio in brackets is not too small, various not-fully-condensed terms will have a contribution to the partition function, meaning that the Taylor series in $V/N\lambda_T^3$ will need to be approximated by more than the first term. These are responsible for the non-condensed fraction. At very low temperature, the fully condensed term is all that remains. (The same kind of reasoning shows, of course, that the normal state will also have non-classical contributions, when close to the critical temperature from above.)

## 5. Discussion

The main proposition of this work is that it may help students to understand Bose-Einstein condensation, if they are exposed to it in a canonical setting, before proceeding to the usual grand-canonical description. Whether this turns out to be so also depends on the former preparation they have received, and on the enthusiasm of the teacher for this sort of explanation.

As to the first, the brief list in the second section of the article gives the formal requirements. In real terms, the students' training should not be entirely on the practical, or computational, side. In particular, the ideas behind the expressions (3) and (6) need to be understood more thoroughly, than is necessary to use them in solving problems.

As to the second, I can only give my own reasons for liking the canonical approach. It gives a good example of using formulae for a qualitative discussion, to predict a real effect before doing any calculation. It helps view the various ensembles as tools, or models of thermodynamics, to be used as convenience dictates, to describe various aspects of a phenomenon. In particular, it provides a simple realistic example, that a phase transition is sharper in temperature, as the system gets larger. Similarly, the discussion of neglected terms below equation (12) gives a fairly good idea, what is a 'critical region' of temperatures around a phase transition. Also, the canonical demonstration emphasizes that Bose-Einstein condensation is a consequence of kinematical, not dynamical, correlations: the example of two bosons makes it obvious, that the quantum terms in equation (5) are there for no other purpose, than the correct book-keeping of indistinguishable particles. Finally, the 'forest' of these extra terms, frightening enough even for three particles (which can be done as an exercise), convinces students to prefer the grand canonical formulation for indistinguishable particles, so they need not take the teacher's word for it.

To conclude, an elementary demonstration of Bose-Einstein condensation has been provided, using the canonical ensemble. Its possible pedagogical advantages are described, relative to the usual grand-canonical description, to which it may serve as an introduction.

## Appendix A. The canonical partition function for non-interacting particles.

One may wonder, what is the general form of equation (4), which can be written

$$Z_C(2,\beta) = \frac{1}{2}\left[Z_C(1,\beta)^2 + Z_C(1,2\beta)\right]. \tag{A.1}$$

In other words, how to express the restricted sum on the left, in general, in terms of the unrestricted sums $Z_C(1,\beta) \equiv z(\beta)$ on the right? To my knowledge, the answer was first published in physicist's terms by Ford [6], though the essential result goes back to di Bruno [7]. The easiest way to derive it is to write the grand partition function (2) as $\exp(\Psi(x))$, where

$$\Psi(x) = \mp \sum_{i=1}^{L} \ln\left(1 \mp x e^{-\beta\varepsilon_i}\right), \tag{A.2}$$

and the upper (lower) sign refers to bosons (fermions). By Taylor's theorem, the $N$-th derivative of $\exp(\Psi(x))$ at $x = 0$, divided by $N!$, is just the canonical partition function. Now one simply takes the formula for the derivative of a composition $f(g(x))$ from a textbook [8]. Putting $f = \exp$ and $g = \Psi$, the result is

$$Z_C(N,\beta) = \sum_{(k)\vdash N} \frac{(\pm 1)^{N+k_1+\ldots+k_N}}{1^{k_1}k_1!\, 2^{k_2}k_2! \cdots N^{k_N}k_N!} z(1\cdot\beta)^{k_1}\cdots z(N\cdot\beta)^{k_N}, \tag{A.3}$$

where $(k) \vdash N$ means all partitions of the number $N$, as denoted by the integers $k_i \geq 0$ :

$$N = 1\cdot k_1 + 2\cdot k_2 + \ldots + N\cdot k_N. \tag{A.4}$$

The partition $k_1 = N$ corresponds to the classical term. The number of partitions of $N$, which is the number of terms in (A.3), grows very rapidly with $N$; for $N = 200$, it is already $\sim 3\times 10^{10}$. Luckily, the result (10) means that for realistic (atomic) masses, typically only a few of these are important, so it is not infeasible to make physical approximations within the canonical approach, for non-interacting particles.

A disadvantage of the above derivation is that a basic recursion [6, 7] is not obvious:

$$Z_C(N,\beta) = \frac{1}{N}\sum_{m=1}^{N} (\pm 1)^{m+1} z(m\beta) Z_C(N-m,\beta). \tag{A.5}$$

However, neither (A.3) nor (A.5) are computationally practical. The really useful recursion is one for canonical occupation probabilities [4], by which all thermodynamic quantities can be calculated numerically exactly, even for a fairly large $N$. It can be derived by differentiating the identity

$$\sum_N x^N Z_C(N,\beta) = \exp\left(\Psi(x)\right) = \exp\left[\sum_{k\geq 1} \frac{(\pm 1)^{k+1}}{k} x^k z(k\beta)\right] \tag{A.6}$$

with respect to a given $\varepsilon_i$, and collecting like powers of $x$. This gives equation (9) of reference [4] directly, circumventing equation (A.5) above.

**Acknowledgments**

This work was supported by the Croatian Government under Project 119 204.

## References

[1] Kittel C 1958 *Elementary Statistical Physics* (New York: Wiley)
[2] Huang K 1963 *Statistical Mechanics* (New York: Wiley)
[3] Cook G and Dickerson RH 1995 *Am. J. Phys.* **63** 737–42
[4] Borrmann P, Harting J, Mulken O and Hilf ER 1999 *Phys. Rev.* **A60** 1519–22
[5] Pathria RK 1996 *Statistical Mechanics, 2nd ed.* (Butterworth-Heinemann) chapter 7
[6] Ford DI 1971 *Am. J. Phys.* **39** 215–20
[7] Faà di Bruno F 1881 *Einleitung in die Theorie der Binären Formen* (Leipzig: B. G. Teubner)
[8] Andrews GE 1976 *The Theory of Partitions* (New York: Addison-Wesley) section 12.3