Bose Condensation and Temperature

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A quantitative analysis of the process of condensation of bosons both in harmonic traps and in gases is made resorting to two ingredients only: Bose classical distribution and spectral discreetness. It is shown that in order to take properly into account statistical correlations, temperature must be defined from first principles, based on Shannon entropy, and turns out to be equal to $\beta^{-1}$ only for $T > T_c$, where the usual results are recovered. Below $T_c$ a new critical temperature $T_d$ is found, where the specific heat exhibits a sharp spike, similar to the $\lambda$-peak of superfluidity.

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In the analysis of low temperature behaviour for Bose systems, temperature is typically thought of as given by $T = 1/k_B \beta$, $\beta$ being the Lagrange multiplier one has to introduce in the customary ensemble approach to account for energy conservation. Such definition however implies in fact the assumption of statistical independence of modes, which not only is not necessary but may even be in contradiction with the basic features of the conceptual scheme leading to the construction of quantum statistics. Indeed, the latter rests on the notion of density matrix, which is correctly introduced only after the Fock space has been properly generated over the tensorized product of the appropriate number of single-particle states. This, in turn, implies the existence of mode correlations which are there even in the absence of interactions. Only when temperature is high enough as to break such correlations, the Fock density matrix can be lifted to a product of single particle density matrices, in which case, however, the only statistics achievable is Maxwell-Boltzmann’s, where correlations are absent.

Ever since 1907 Einstein himself \cite{Einstein}, discussing the behavior at low temperature of the quantized harmonic oscillator in the frame of Boltzmann statistics, pointed out how classical results on equipartition of energy are, in agreement with the Nernst theorem, no longer valid for $T < h \nu/k_B$, by obtaining a good fit of the heat capacity data for diamond. One of his basic assumptions was the extensivity hypothesis. The latter is usually transferred, adopting a tensor product structure for the Hilbert space of states of a multi-particle system, to the whole Quantum Statistical Mechanics (QSM) in spite of the fact that it can be justified for the Gibbs-Boltzmann distribution only, related in this case to the statistical independence of different modes. It worked well for Einstein when he dealt with the carbon atoms in diamond (which of course do not condense) in that, being fixed at their positions in the crystal, these are distinguishable, while one of the characteristic features of quantum mechanics is indistinguishability of the particles.

Several authors have discussed Bose Einstein condensation (BEC) in magnetic traps, all on the basis of that same definition of temperature \cite{Leggett}, \cite{Dippenaar}, \cite{Smerzi}, finding – together with $T_c \propto N^{1/3}$ – a heat capacity monotonically decreasing to zero for $T$ below $T_c$, in agreement with what happens for true gases under the same hypotheses.

On the other hand Bose, when he “invented” bosons, broke scale invariance in the same way as Democritus did in the 5th century BC: because of correlations, a condensate is not the disjoint union of smaller condensates, in the same way as an atom (ancient or modern) is not equal to two half-atoms. The properties of a condensate do depend on the number $N$ of atoms it contains, as one cannot consider the thermodynamic limit \cite{Zwanzig}, \cite{Dorey}, \cite{Dalibard} that would require, together with $N \to \infty$, $h \nu \propto N^{-1/3}$ (i.e. the continuum), in conflict with the properties of magnetic traps where the spectrum (discrete) has a spacing which is fixed and comparable with $k_B T_c$. In other words the distinction of physical quantities in intensive and extensive is not consistent with Bose-Einstein condensation, as proved, among others, by the mentioned relation $T_c \propto N^{1/3}$.

All these well known features are little relevant for $T > T_c$, because the particles there are distributed over all levels, and the continuum approximation appears to be sufficient both for describing the regime for $T > T_c$ and for determining $T_c$ itself (minor corrections may arise, that will be considered elsewhere \cite{Note}). However, as soon as the condensate fraction $c = \overline{\pi}_0/N$ becomes relevant ($T < T_c$), statistics becomes significantly different from Boltzmann’s and the very definition of temperature must be reconsidered together with, but independently from, the question of equipartition. Temperature can be defined, in a quite general and basic way, in terms of two fundamental physical quantities; internal energy $E$ and entropy $S$. Thus instead of connecting $T$, because of extensivity, to the Lagrange multiplier $\beta$, one can derive it from the separate measurements of $E$ and $S$.

We shall then consider \textit{ab initio}, in the grand-canonical ensemble, a system of $N$ bosons of total energy $E$ and we shall explicitly evaluate the Lagrange multipliers as functions of $N$ and $E$. Successively, Shannon’s form of entropy will be our starting point to derive all equilibrium
thermodynamic properties. In other words, our hypotheses will be the three consistent assumptions:

a) The Bose-Einstein statistics:

\[ \pi_i = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}, \]  

b) a discrete energy spectrum (as suggested by the typical experimental set-up with magnetic traps, where \( k_B T_c \approx 10 h \nu \)), and
c) Shannon entropy, evaluated in terms of \( N \) and \( E \).

Temperature \( T = T(N,E) \) will then be obtained as a derived quantity by \( T = \partial E / \partial S \).

![Specific heat C/kB vs. T/Tc for N = 10^6 bosons in an isotropic harmonic trap, as predicted by the entropy approach.](image)

In this way the correlations induced by quantum statistics enter into play only in the definition of the \( p_i \)'s which are such that \( p_i = N_i / N \approx 1/2 \), at which it exhibits a sharp spike, analogous to that of superfluids. As no interaction has been introduced, other than the confining potential, this enhance the idea that superfluid transition may indeed be ascribable, as originally suggested by Onsager and Penrose, essentially to Bose-Einstein condensation. For \( T < T_d \), specific heat goes to zero when \( T \) goes to zero, in agreement with Nernst’s theorem. It is suggestive that, for \( T \rightarrow 0, C \propto T^3 \) for harmonic traps whereas \( C \propto T^{3/2} \) for bosons in a box. In Fig.1 \( C/k_B \) is given vs. the “probabilistic” temperature. To check the procedure, \( C \) has also been numerically evaluated as \( \partial E / \partial \beta^{-1} \), checking that this coincides with the standard textbook form (see, e.g., [12]). It is thus clear that the effect lies in the different definitions of temperature and not in computations.

We shall now summarize a few technicalities of the procedure, emphasizing that the scheme proposed to deal with correlations could in principle be utilized also for interactions.

1) A set of values for \( N \) in the range \( 10^6 \div 10^9 \) as well as a set of values for the mean energy per particle \( E/N \) in the range from the ground state up to \( 10^4 \) units \( h \nu \) for the magnetically trapped system and \( h^2/L^2 \) for the cubic box (of side \( L \)) have been considered. The difference between the two cases lies in the energy spectrum and its level multiplicity. The full range of condensation \( 0 < c \equiv \pi_0/N < 1 \) has thus been covered.

2) For each pair of values \( N \) and \( E \) the system of two equations in the two unknowns \( \alpha \) and \( \beta \):

\[ \sum \pi_i(\alpha, \beta) = N, \quad \sum \epsilon_i \pi_i(\alpha, \beta) = E, \]

(in the sums the correct state multiplicities have of course been taken into account) was solved. The two functions \( \alpha = \alpha(N,E) \) and \( \beta = \beta(N,E) \) were thus found.

3) Successively, the \( \pi_i = \pi_i(N,E) \) were obtained from eq. (1). In particular the condensate fraction \( c = \pi_0/N \) was determined as a function of \( N \) and \( E \).

4) The probability of finding a particle in state \( i \), picking it up at random in the ensemble is \( p_i(N,E) = \pi_i/N \). This allows us, adopting Shannon’s definition, to find the entropy \( S \) as a function of \( N \) and \( E \):

\[ S = -k_B \sum p_i \ln p_i. \]

In this way the correlations induced by quantum statistics enter into play only in the definition of the \( p_i \)’s which are such that \( p_i^{(1,2)} \neq p_i^{(1)} p_i^{(2)} \) if the system is split into the union of two parts. It is interesting to note that, had we considered Boltzmann distribution and not eq. (1), Gibbs’ distribution would have been obtained and the results of [1] reproduced. Once the \( p_i \)’s are known, any further analysis of equilibrium thermodynamical properties is mere statistics.

5) Temperature \( T \) is obtained, as a function of \( N \) and \( E \), by numerical derivation:

\[ T = T(N,E) = \left( \frac{\partial E}{\partial S} \right)_N. \]

6) The relation \( T = T(N,E) \) is monotonic in \( E \) for fixed \( N \), and it can be inverted to obtain \( E = E(N,T) \), whence the specific heat is obtained by (numerical) differentiation (see Fig. 1):
\[ C \equiv \left[ \frac{\partial(E/N)}{\partial T} \right]_N \].

7) "Probabilistic" temperature \( T \), despite its conceptual relevance, is perhaps not the physical parameter that best describes the process of condensation: it is difficult to measure in the experimental set-up of traps and, as one does not have equipartition, its intuitive meaning of "average energy per particle" is lost. On the other hand, experimentalists define temperature deriving it from the high energy tail of the velocity distribution for which they assume \( \text{equipartition} \). In other words, the "experimental" temperature is

\[ \Theta := \frac{1}{3k_B N} \frac{1}{N} \sum_{j \neq 0} n_j \epsilon_j. \]

We therefore describe the onset of condensation by exhibiting the behavior of \( c \equiv n_0 / N \) vs. \( \Theta \) (Fig. 2), that we compare with \( c \) vs. \( T \) (Fig. 3).

![Fig. 2. Condensate fraction \( c \equiv n_0 / N \) vs. "experimental" temperature \( \Theta / T_c \). The curve is perfectly fitted by \( c = 1 - (\Theta / T_c)^3 \).](image)

For the sake of completeness, we report also the "experimental" specific heat \( C \equiv \frac{\partial(E/N)}{\partial \Theta} \) (Fig. 4). It should be noticed that since above critical temperature equipartition holds also in our case, the two critical temperatures coincide \( (\Theta_c \equiv T_c \approx 9\hbar \nu / k_B N^{1/3}) \) and equal that given in \( [3] \). In Fig. 5 the specific heat of the "warm tail", \( C_w \equiv \frac{\partial(3k_B \Theta)}{\partial T} \) is shown vs. \( T / T_c \).

8) As we have the complete description of the system in function of \( N \) and \( E \), all physical observables can be obtained. For instance the chemical potential, \( \mu \equiv \mu(N, E) = \frac{\partial E}{\partial \mu} \), which gives \( \alpha \neq -\beta \mu \).

In order to make the figures more easily comparable with known results in the literature, only those referring to a single value of \( N \) \( (N = 10^9) \) and to the harmonic confining trap are reported. It should be pointed out that, taking into account that \( T_c \propto N^{1/3} \), no substantial differences appear either for different values of \( N \) nor for the gas in a box.

![Fig. 3. \( c \) vs. \( T / T_c \) (\( T \) probabilistic temperature). Apparently similar to Fig. 2, just merging to zero in a smoother way, this is indeed deeply different, in that the critical temperature is \( T_d \) instead of \( T_c \).](image)

![Fig. 4. "Experimental" specific heat \( C / k_B \equiv \frac{\partial(E/N)}{\partial(k_B \Theta)} \) vs. \( \Theta / T_c \). Well reproduces the result in \([5]\).](image)

Our interest is focussed on different aspects. On the one side the proposed combinatorial approach emphasizes the relevance, for a proper interpretation of phenomenological data, of a definition of temperature adequate to the experimental set up. On the other, it hints to the existence at very low temperature of effects that would be worth investigating in the laboratory. Such effects are probably at present beyond reach, but experiments are in constant evolution, and the effort might open interesting new perspectives. Finally, it may provide a novel insight on the \( \lambda \)-transition in superfluids.

QSM has always been at the border between statistical mechanics (SM) and probability theory. For the latter [13] SM is related to information theory, where also the lexicon is different from that usual one in physics. For instance, "Boltzmann statistics" is simply the common limit for \( n_i \ll 1 \) of the only two existing statistics, Bose and Fermi in [14], while is just one possible "physical distribution" with unlimited occupation numbers, like that of Bose in [13], [15].
In distribution theory all information is contained in weights such as those in eq. (8), while the fundamental hypothesis of statistical mechanics is statistical independence of the subsystems. In QSM it is the symmetrization imposed by particle indistinguishability that one has to perform, e.g. moving to Fock space, that breaks such independence. Results of physical interest are nevertheless typically in agreement, which is due in most cases to the fact that statistical correlations are irrelevant and therefore all physical distributions are equivalent. Well established exceptions are fermions at low temperature and, referring to bosons, the black body, where photons are well described by eq.(9). In black body theory, however, the situation is very peculiar because photons essentially cannot interact with each other.

On the other hand, in view of the continuous improvements of experimental techniques, extending QSM to describe experiments where \( \pi_i \neq 1 \), the spectrum is discrete, the number of particles and modes is large but not so large as to allow a continuum description, is certainly a challenge that will have to be faced soon. Indeed all of this is already happening just for one physical set-up: Bose condensation in magnetic traps.

In the condensate most particles are in the fundamental level and, in typical experimental situations, \( k_B T_c \) is only of the order of ten times the spectrum spacing (\( T_c \approx 10^2 nK, \hbar \nu/k_B \approx 10 nK \)). The usual approximation in terms of continuum density with \( \pi_0 \) obtained by difference, appears to be improvable. Moreover, the statistical independence of levels – acceptable in the black body – is questionable when the container is a magnetic field and has no kind of thermal exchange with the atoms. Thermodynamic equilibrium of each mode is reached because not of the interaction of the mode itself with the bath, but of the jumping of atoms from one level to another, as clearly shown by the fast restoring of equilibrium after each cooling. In the case of gas, temperature is controlled by the walls and the physics of thermalization is different but, if the statistics is that of Bose, statistical independence must be excluded.

Keeping the spectral structure into account provides the correct conceptual scheme as opposed to a theory where continuum and equipartition are assumed \( a \ priori \). On the other hand, many body effects so far not considered should be analysed; however we expect that including in the picture interactions in the ground state, as described in the Gross-Pitaevsky approach \([8, 9]\), may modify at most the energy spectrum, and the ensuing differences in numerical values should not be able to substantially mask the effects discussed.

It should be pointed out that the description presented, based on the assumption of spectral discreteness, leads not only to qualitative behaviours, but it determines as well physical observables: specific heat, filling order parameter, chemical potential, etc., all of which can be experimentally measured, related to the characteristics of the experiment \( (N, E, \nu) \). To this effect, it should be observed that in real experiments the harmonic potential is usually anisotropic: extension of our results to this situation is straightforward and leads to quite similar predictions.

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