Canonical and microcanonical ensemble approaches to Bose-Einstein condensation: The thermodynamics of particles in harmonic traps

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Abstract. The thermodynamic properties of bosons moving in a harmonic trap in an arbitrary number of dimensions are investigated in the grand canonical, canonical and microcanonical ensembles by applying combinatorial techniques developed earlier in statistical nuclear fragmentation models. Thermodynamic functions such as the energy and specific heat are computed exactly in these ensembles. The occupation of the ground or condensed state is also obtained exactly, and signals clearly the phase transition. The application of these techniques to fermionic systems is also briefly discussed.

PACS. 03.75.Fi Phase coherent atomic ensemble (Bose condensation)

1 Introduction

Recently there has been a renewed interest in the thermodynamics of mesoscopic systems. In particular, the experimental observation of condensation phenomena in nanokelvin aggregates of atoms moving in magnetic traps [1–4] has encouraged a number of theoretical investigations of this phenomenon [5–7] extending earlier investigations [8–10]. These works assume that the systems can be adequately described by the grand canonical ensemble in which both the energy and particle number are allowed to fluctuate, and use the harmonic oscillator potential as suggested in [11]. The canonical ensemble is probably more representative of the experimental conditions and has also been investigated [12–15].

In this work, we analyze the thermodynamics of bosons in the the grand canonical, canonical and microcanonical ensembles by applying particularly effective techniques that two of us have used before in describing nuclear systems statistically [16–18]. This reproduces the recursive formula for the canonical partition function from a combinatorial argument which proffers several advantages over the earlier purely functional treatment [12]. In particular, this interpretation enables a simple and exact determination of the expected occupancies of the energy levels in any of the ensembles. This allows the usual thermodynamic functions to be expressed exactly and succinctly, not just the partition function. Additionally, the method is related to the permutational decomposition of the liquid ^{4}He partition function proposed by Feynman [19,20]. Previously, we have used this correspondence to specify

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partition functions for isotopic nuclear systems [21]. In this paper, the correspondence enables as a new result an exact determination of the microcanonical partition function.

2 The partition function for identical bosons or fermions

In statistical mechanics the partition function entirely specifies the thermodynamics, so our first priority is to determine a method of computing the partition function in the various ensembles. We begin by considering the grand canonical partition function, and develop a combinatorial method of extracting the canonical and microcanonical partition functions from the larger ensemble. In the process we develop exact expressions for the expected occupation of the energy levels in all three ensembles.

2.1 Grand canonical partition function

In the grand canonical ensemble, where the particle number and energy are unconstrained, the partition function Z for a system of bosons occupying energy levels ε_k with degeneracy g_k is given by

$$\ln Z = -\sum_{j \geq 0} g_j \ln \left(1 - e^{(\mu - \varepsilon_j)/k_B T} \right), \qquad (1)$$

where μ is the chemical potential. Let us think of this as a sum either over canonical Z_n or microcanonical $Z_{n,E}$

partition functions, *i.e.*

$$Z = \sum_n z^n Z_n = \sum_{n,E} z^n w^E Z_{n,E}, \qquad (2)$$

where the fugacity z is given by $z = \exp\{\mu/k_B T\}$ and $w = \exp\{-1/k_B T\}$. Expanding equation (1) as a power series in z, w yields

$$\begin{aligned}
\ln Z &= \sum_{j=0}^{\infty} g_j \sum_{k=1}^{\infty} \frac{z^k}{k} w^{k\varepsilon_j} \\
&= \sum_{k=1}^{\infty} z^k x_k = \sum_{k=1}^{\infty} \sum_{j=0}^{\infty} z^k w^{k\varepsilon_j} x_{jk},
\end{aligned} \qquad (3)$$

where we have introduced $x_{jk} = g_j/k$ and $x_k = \sum_j w^{k\varepsilon_j} x_{jk}$ for reasons which will become clear shortly. If we exponentiate and Taylor expand equation (3) we see that

$$\begin{aligned}
Z &= \sum_{\pi_{01}=0}^{\infty} \frac{(zw^{\varepsilon_0} x_{01})^{\pi_{01}}}{\pi_{01}!} \sum_{\pi_{02}=0}^{\infty} \frac{(z^2 w^{2\varepsilon_0} x_{02})^{\pi_{02}}}{\pi_{02}!} \times \cdots \\
&= \sum_{\{\pi_{jk}\}} \prod_{jk} \frac{(z^k w^{k\varepsilon_j} x_{jk})^{\pi_{jk}}}{\pi_{jk}!},
\end{aligned} \qquad (4)$$

where $\pi_{jk} \geq 0$.

Notice that the exponents of w, z in equation (4) are simple functions of $\{\pi_{jk}\}$. Since the exponent of w in the grand canonical partition function is the total energy E in the particular microcanonical component, the exponent of w, $\sum_k k\varepsilon_j \pi_{jk}$ should be equal to the energy E for that particular state $\{\pi_{jk}\}$. This $E = \sum_j n_j \varepsilon_j$, where n_j is the number of particles in energy state j, so the state $\boldsymbol{\pi}$ is related to $\boldsymbol{n}$ by

$$n_j = \sum_k k\pi_{jk}. \qquad (5)$$

Combinatorially speaking, π_{jk} counts collections of k particles in the jth energy state. In fact, $\{\pi_{jk} : j \text{ fixed}\}$ is simply a cycle class decomposition of a permutation of the n_j particles in the jth energy level. To see this, consider the part of the grand canonical partition function due to energy level j, namely the number of states of a system with n_j bosons in a level with degeneracy g_j,

$$\begin{aligned}
\binom{n_j + g_j - 1}{n_j} &= \sum_{\{\pi_{jk} : j \text{ fixed}\}} \prod_k \frac{1}{\pi_{jk}!} \left(\frac{g_j}{k}\right)^{\pi_{jk}} \\
&= \frac{1}{n_j!} \sum_{p \in S_{n_j}} \prod_k g_j^{\pi_{jk}(p)}.
\end{aligned} \qquad (6)$$

Here we see that $\binom{n_j+g_j-1}{n_j}$ can be described in two ways. The first is just the isolated contribution from the above grand canonical partition function. The second is a sum over permutations of the n_j particles, where $\pi_{jk}(p)$ is the number of k-cycles in the permutation p of n_j.

The equivalence of these two expression is due to Cauchy and Sylvester [22].

Feynman considered such permutations in the condensation of liquid ^{4}He [20] and was able to obtain a form for the partition function by expanding the symmetrized density matrix as a sum over such permutations. Specifically, the sum $\pi_k = \sum_j \pi_{jk}$, the total number of cycles of length k, figures prominently in Feynman's approach. Such permutational decomposing of the partition function has also been useful in our research on isotopic nuclear systems [21], where the dual requirement of proton and neutron conservation was considered as restricting the permutational states to have been colored in a particular way. Here we can accomplish a similar interpretation by coloring the clusters which form according to the energy levels they reside in. Parallels of permutation problems with cluster yields were also noted in [17,18].

Since π_{jk} has a combinatorial interpretation and is related to n_j, it is important to obtain expectation values of it. This is possible since each term of equation (4) can be interpreted as an unnormalized probability for the state $\{\pi_{jk}\}$, the normalization being simply the partition function. Equation (4) then suggests we can evaluate such expectation values of π_{jk} by taking various derivatives of the partition function. More specifically, it is true that $\langle \pi_{jk} \rangle = (x_{jk}/Z)(\partial Z/\partial x_{jk})$ and $\langle \pi_{jk}(\pi_{lm} - \delta_{jk,lm}) \rangle = (x_{jk} x_{lm}/Z)(\partial^2 Z/\partial x_{jk} \partial x_{lm})$, where $\langle \cdot \rangle$ denotes a grand canonical ensemble average. Now according to equation (3), $Z = \exp \sum_{jk} z^k w^{k\varepsilon_j} x_{jk}$, so that

$$\frac{\partial Z}{\partial x_{jk}} = z^k w^{k\varepsilon_j} Z(\mathbf{x}). \qquad (7)$$

We then see that

$$\langle \pi_{jk} \rangle = z^k w^{k\varepsilon_j} x_{jk}, \qquad (8)$$

$$\langle \pi_{jk}(\pi_{lm} - \delta_{jk,lm}) \rangle = z^{k+m} w^{k\varepsilon_j + m\varepsilon_l} x_{jk} x_{lm}. \qquad (9)$$

We can now "solve" the grand canonical partition function now by using the combinatorial interpretation to specify w, z, *i.e.* by applying the constraints $n = \sum_j \langle n_j \rangle = \sum_{jk} k\langle \pi_{jk} \rangle$, $E = \sum_j \langle n_j \rangle \varepsilon_j = \sum_{jk} k\langle \pi_{jk} \rangle \varepsilon_j$.

The analysis illustrated above for a system of bosons applies equally well to a system of fermions. In this case, the appropriate partition function is

$$\ln Z = \sum_j g_j \ln(1 + e^{(\mu - \varepsilon_j)/k_B T}). \qquad (10)$$

Expanding this yields equation (3) with $x_{jk} = (-1)^{k+1} g_j/k$. The fact that x_{jk} can be negative means that the combinatorial interpretation is somewhat suspect, since some contributions to the partition function are negative. Nevertheless, the mathematics is sound and expectation values of $\langle n_j \rangle$ can be computed correctly by the same technique used above. This fermionic case will be discussed in detail in another paper.

2.2 Canonical partition function

We can obtain the canonical partition function from the grand canonical partition function by making restrictions on the sum appearing in equation (4), *i.e.* if we restrict the sum to terms where $n = \sum_{jk} k\pi_{jk}$ we will obtain the canonical partition function. We could simplify some of the computations by defining $\pi_k = \sum_j \pi_{jk}$, so that the states are described by $\{\pi_k\}$ where $\sum_k k\pi_k = n$. Mathematically speaking, such vectors $\{\pi_k\}$ describe partitions of the integer n [22], where π_k is the number of time k appears in such a partition. However, sometimes it is more convenient to work instead with π_{jk}.

Let us define $\pi(n) = \{\pi_{jk} : \sum_{jk} k\pi_{jk} = n\}$. Then the canonical partition function is given by

$$Z_n(\mathbf{x}) = \sum_{\pi(n)} \prod_{k>0} \frac{(w^{k\varepsilon_j} x_{jk})^{\pi_{jk}}}{\pi_{jk}!} . \qquad (11)$$

Since $\sum_{jk} k\pi_{jk} = n$ for each state in the ensemble, it is true that $\sum_{jk} k\langle \pi_{jk}\rangle_n = n$, where $\langle \cdot \rangle_n$ denotes a canonical ensemble average. The canonical ensemble average for π_{jk} can be computed by taking a derivative of the partition function $\langle \pi_{jk}\rangle_n = (x_{jk}/Z_n)(\partial Z_n/\partial x_{jk})$ as can be seen from equation (11). In terms of the canonical partition functions, the canonical constraint can be rewritten then as

$$nZ_n(\mathbf{x}) = \sum_{k=1}^{n} k \sum_{j\geq 0} x_{jk} \frac{\partial Z_n}{\partial x_{jk}} . \qquad (12)$$

If we could relate $\partial Z_n/\partial x_{jk}$ to $Z_1(\mathbf{x})$, $\ldots$, $Z_{n-1}(\mathbf{x})$ then the above identity would imply a recursive method for computing $Z_n(\mathbf{x})$.

In fact $\partial Z_n/\partial x_{jk}$ is precisely proportional to a particular partition function as can be seen by combining equation (7) and equation (2), yielding

$$\frac{\partial Z_n}{\partial x_{jk}} = w^{k\varepsilon_j} Z_{n-k}(\mathbf{x}). \qquad (13)$$

So the identity given in equation (12) is in fact a recursion for construction the partition function:

$$nZ_n(\mathbf{x}) = \sum_{jk} kx_{jk} w^{k\varepsilon_j} Z_{n-k}(\mathbf{x}) = \sum_k kx_k Z_{n-k}(\mathbf{x}), \qquad (14)$$

with $Z_0(\mathbf{x}) = 1$ as the anchor for the recursion. The expectation values for π_{jk} are simply related to the partition functions:

$$\langle \pi_{jk}\rangle_n = w^{k\varepsilon_j} x_{jk} \frac{Z_{n-k}(\mathbf{x})}{Z_n(\mathbf{x})}, \qquad (15)$$

$$\langle \pi_{jk}(\pi_{lm} - \delta_{jk,lm})\rangle_n = w^{k\varepsilon_j + m\varepsilon_l} x_{jk} x_{lm} \frac{Z_{n-k-m}(\mathbf{x})}{Z_n(\mathbf{x})} . \qquad (16)$$

2.3 Microcanonical partition function

A similar combinatorial argument can extract the microcanonical partition function from the canonical or grand canonical partition function. Let us define $\pi(n, E) = \{\pi_{jk} : \sum_{jk} k\pi_{jk} = n, \sum_{jk} k\varepsilon_j \pi_{jk} = E\}$. Then

$$Z_{n,E}(\mathbf{x}) = \sum_{\pi(n,E)} \prod_{jk} \frac{x_{jk}^{\pi_{jk}}}{\pi_{jk}!}. \qquad (17)$$

The partition function can now be developed by recursion by noting that

$$\langle \pi_{jk}\rangle_{n,E} = x_{jk} \frac{Z_{n-k,E-k\varepsilon_j}(\mathbf{x})}{Z_{n,E}(\mathbf{x})}, \qquad (18)$$

$$\langle \pi_{jk}(\pi_{lm} - \delta_{jk,lm})\rangle_{n,E} = x_{jk} x_{lm} \frac{Z_{n-k-m,E-k\varepsilon_j - m\varepsilon_l}(\mathbf{x})}{Z_n(\mathbf{x})}, \qquad (19)$$

and applying the identity $\sum_{jk} k\langle \pi_{jk}\rangle_{n,E} = n$, yielding

$$nZ_{n,E}(\mathbf{x}) = \sum_{jk} kx_{jk} Z_{n-k,E-k\varepsilon_j}(\mathbf{x}), \qquad (20)$$

with $Z_{0,E}(\mathbf{x}) = \delta_{0,E}$.

A similar situation arises in models of nuclear fragmentation, where there is also two constraints, namely the conservation of proton and neutron number, in which case [21] it is useful to restrict the ensemble by summing over isotopes or isobars. Then the existence of permutational Cauchy identities simplified the resulting partition functions. In this case the same kind of mechanism also applies. We can sum over the energy states and arrive at the π_k cluster representation of the states. Or we can sum over the cluster sizes and arrive at the n_j occupation number representation. In each case, the weight retains its form and the analysis in the restricted space is identical or nearly identical as in the large space.

3 Application to the harmonic oscillator

Having the partition function now allows us to compute the thermodynamics in the traditional manner. For the case of particles moving in a d dimensional isotropic harmonic potential, g_j and ε_j can be evaluated directly. The Hamiltonian for the system is given by $\hat{H} = \sum_{i=1}^{d} p_i^2/2m + m\omega^2 \sum_{i=1}^{d} q_i^2/2$ where (q_i, p_i) is the position and momentum in the ith direction. So $H = \sum_i H_i$ where H_i is the Hamiltonian for a one-dimensional oscillator acting on (q_i, p_i). Of course $H_i\psi_n(q_i) = (n + 1/2)\hbar\omega\psi_n(q_i)$, and by separation of variables $H\psi_{n_1, \ldots, n_d} = (n_1 + \cdots + n_d + d/2)\hbar\omega\psi_{n_1, \ldots, n_d}$. If we write this as simply $\varepsilon_j = (j + d/2)\hbar\omega$, we see that the jth energy level has a degeneracy g_j based on the number of ways one can write j as an ordered sum of d nonnegative integers, *i.e.* $j = n_1 + \ldots + n_d$. In combinatorics this is known as a d-composition of j, and there are $g_j = \binom{j+d-1}{j}$ ways
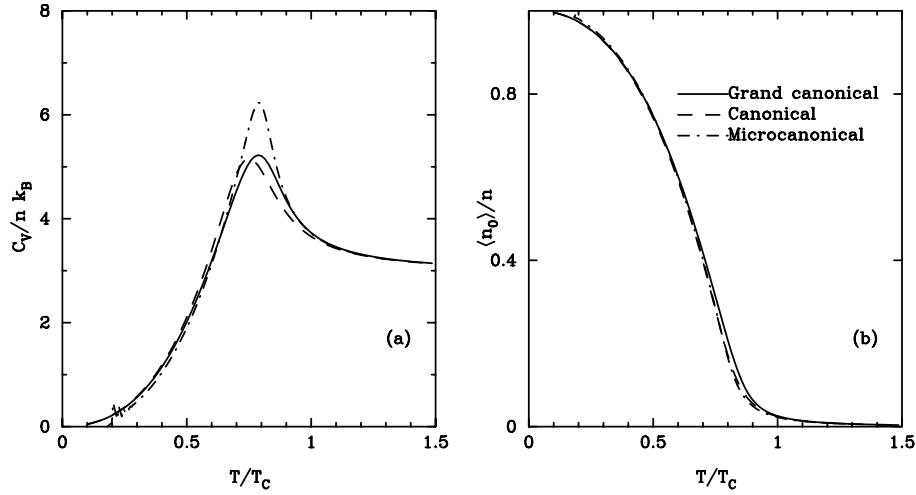
Fig. 1. The specific heat and ground state occupation in three dimensions in the grand canonical, canonical and microcanonical ensembles for a system of 100 particles. The curves become nearly identical for larger groups of particles.

of doing this. Substituting this into $x_k = (1/k) \sum_j g_j w^{k\varepsilon_j}$ yields

$$x_k = \frac{1}{k} \sum_{j=0}^{\infty} \binom{j+d-1}{j} x^{k(j+d/2)} = \frac{1}{k} \frac{x^{kd/2}}{(1-x^k)^d}, \quad (21)$$

where $x = \exp\{-\hbar\omega/k_B T\}$ and we have applied the negative binomial identity $(1-x)^{-d} = \sum_{n \geq 0} x^n \binom{n+d-1}{n}$.

3.1 Canonical thermodynamics

We can now compute the canonical partition function for the harmonic oscillator recursively using equation (12). Of interest is the fact that in one dimension the recursion yields a particularly simple form due to a partition theorem of Cayley (cf. [22], 209), namely: $Z_{n,d=1}(x) = x^{n/2}/((1-x)(1-x^2)\cdots(1-x^n))$. This partition function was investigated in a different context by Mekjian and Lee [23]. In two and higher dimensions, the partition function does not have a simple closed form, but can be computed by the above recursion.

Having obtained the partition function we can compute any thermodynamic function of interest by a judicious use of partial derivatives. For example, in the canonical ensemble, the internal energy $U = k_B T^2 (\partial/\partial T)_V \ln Z_n$ and the specific heat $C_V = (\partial U/\partial T)_V$ for a group of bosons are given by

$$\frac{U}{k_B T} = \sum_{k>0} \frac{T}{x_k} \frac{\partial x_k}{\partial T} \langle \pi_k \rangle_n, \quad (22)$$

$$\frac{C_V}{k_B} = \frac{2U}{T} + \left[\sum_{k>0} \left(\frac{T^2}{x_k} \frac{\partial^2 x_k}{\partial T^2} - \left(\frac{T}{x_k} \frac{\partial x_k}{\partial T} \right)^2 \right) \langle \pi_k \rangle_n \right.$$
$$\left. + \sum_{jk} \frac{T}{x_j} \frac{\partial x_j}{\partial T} \frac{T}{x_k} \frac{\partial x_k}{\partial T} \left(\langle \pi_j \pi_k \rangle_n - \langle \pi_j \rangle_n \langle \pi_k \rangle_n \right) \right]. \quad (23)$$

The pressure $P = k_B T (\partial/\partial V)_T \ln Z_n$ and the incompressibility $1/\kappa_T = -V(\partial P/\partial V)_T$ can be computed in a similar fashion. For the harmonic oscillator, the partial derivatives of x_k with respect to T are readily determined. The partial derivatives with respect to V can also be determined, once an appropriate volume is specified. Since $\hbar\omega$ determines the size of the trap, $\hbar\omega$ determines the volume. Assuming $h^2/2m\lambda^2 \approx m\omega^2\lambda^2/2$ where λ is a particle's wavelength we see that $\hbar\omega \propto V^{-2/d}$.

For computational purposes, the above expressions are concise and powerful, but for understanding the source of the phase transition, one needs to rewrite the above expressions in terms of the occupancies of the levels. Since $Z_n = \sum_{\mathbf{n}} Z_{\mathbf{n}} \exp\{-\sum_j n_j/k_B T\}$ it can be shown that $U = \sum_j \langle n_j \rangle_n \varepsilon_j$, and that $C_V = \sum_{jk} (\langle n_j n_k \rangle_n - \langle n_j \rangle_n \langle n_k \rangle_n) \varepsilon_j \varepsilon_k/(k_B T^2)$. As the critical point is marked by a peak in the specific heat, from the above expression its source must be due to large fluctuations in the occupation numbers. The expected occupation numbers can be inferred from equations (5, 15, 16), yielding

$$\langle n_j \rangle_n = g_j \sum_k w^{k\varepsilon_j} \frac{Z_{n-k}(\mathbf{x})}{Z_n(\mathbf{x})}, \quad (24)$$

$$\langle n_j n_k \rangle_n = \delta_{jk} g_j \sum_m m w^{m\varepsilon_j} \frac{Z_{n-m}(\mathbf{x})}{Z_n(\mathbf{x})}$$
$$+ g_j g_k \sum_{lm} w^{l\varepsilon_j + m\varepsilon_k} \frac{Z_{n-l-m}(\mathbf{x})}{Z_n(\mathbf{x})}, \quad (25)$$

and allow the expected occupation and its fluctuation to be computed readily.

3.2 Microcanonical thermodynamics

In the microcanonical ensemble, the temperature is defined by $T = (\partial E/\partial S)_{n,V}$, and this allows us to compute

the thermodynamic functions, *e.g.* for the harmonic oscillator

$$C_V = -\frac{(S_{n,E+\hbar\omega} - S_{n,E})(S_{n,E} - S_{n,E-\hbar\omega})}{S_{n,E-\hbar\omega} - 2S_{n,E} + S_{n,E+\hbar\omega}}, \qquad (26)$$

where $S_{n,E} = \log Z_{n,E}$. Relating the thermodynamics to the occupancies of the levels is more difficult than in the canonical case, since the temperature is not an independent parameter.

4 Discussion and conclusion

As an application of the above techniques, we display the thermodynamics of particles in a harmonic trap in the three ensembles. The specific heat (Fig. 1a) and the occupation of the ground state (Fig. 1b) are substantially in agreement in all three ensembles, confirming the essential validity of the use of the different ensembles even for such small groups of particles. The finite size effects are however measurable, and should not be completely discounted, especially in smaller systems.

In summary, we have introduced a combinatorial approach to computing thermodynamic functions in systems of identical bosons. It is ideally suited to systems in which the energy levels are separated by integral multiples of some fundamental energy, such as in the harmonic oscillator ($\varepsilon_j = j\hbar\omega$) and the rigid rotator ($\varepsilon_j = j(j+1)\hbar^2/2I$). Such techniques can also be applied to groups of identical fermions, which has applications to the nuclear shell model at finite temperatures.

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