

Canonical versus Grand Canonical Occupation Numbers for Simple Systems

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Ihr naht euch wieder,
schwankende Gestalten,
Die früh sich einst dem
trüben Blick gezeigt.
Versuch ich wohl, euch
diesmal festzuhalten?
Fühl ich mein Herz noch
jenem Wahn geneigt?
Ihr drängt euch zu! Nun gut,
so mögt ihr walten,
Wie ihr aus Dunst und Nebel,
um mich steigt.

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An ideal gas of N indistinguishable particles is described by a canonical ensemble (c.e.) and also by a grand canonical ensemble (g.c.e.) which has N as the mean total number of particles, the temperature and volume being the same in both cases. Exact mean occupation numbers $n_j(N)$ are found if the system has only two states 1 and 2 of energies $E_2 \geq E_1$. This should apply to quantum wells and similar simple systems. For systems which have captured one particle, the theory gives the simplest answers, and one finds a maximum discrepancy of 17% between the two ensembles for the fermion case. It occurs when $E_2 - E_1 \sim 53$ meV at room temperature. For $N = 1$ the mean occupation number for the c.e. is identical for fermions and for bosons, being in both cases given by $n_2(1) = \{\exp[(E_2 - E_1)/kT] + 1\}^{-1}$, $n_1(1) = 1 - n_2(1)$. For large N one reverts to the usual situation and the discrepancy between the ensembles becomes small.

KEY WORDS: Ideal quantum gas; fermions; bosons; canonical ensemble; grand canonical ensemble; occupation numbers.

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1. INTRODUCTION

Suppose a quantum well has two localized states and it has captured N electrons. With microelectronic devices becoming ever smaller, small values of N come within the range of possibilities and we shall concentrate here on the case $N=1$. What are the equilibrium mean occupation numbers $n_j(N)$ of the two states 1 and 2 ($E_2 > E_1$)? One answer is

$$n_j = [\exp(\eta_j - \gamma) \pm 1]^{-1}, \quad j = 1, 2 \quad (1.1)$$

where $\gamma \equiv \mu/kT$, $\eta_j = E_j/kT$, T is the temperature of the system, and μ is the chemical potential. But we had specified the number of particles N in the system, not the chemical potential. Hence (1.1), being based on the grand canonical ensemble (g.c.e.), is inappropriate, even though everybody thinks of it as *the* Fermi (or Bose) distribution function. A second approach is to state the canonical ensemble (c.e.) result for T and N

$$n_j(N) = \left[\frac{Z_{n+1} n_j(N+1)}{Z_N n_j(N)} e^{\eta_j} \pm 1 \right]^{-1} \quad (1.2)$$

where Z_N is the partition function of the system for N particles with point interactions. The volume v is also given for (1.1) and (1.2). But (1.2) is merely a recurrence relation which still has to be solved for $n_j(N)$. It goes over into (1.1) only if an approximation is made; for example, one may assume $n_j(N+1)/n_j(N) \sim 1$.

In fact, fairly involved relations have been obtained in the past in a determined quest to find out precisely, and without approximation, what the c.e. really tells us about even as simple a system as an ideal gas. But one has to make do with (1.2) or with inequalities. The latter are rather delicate in this case, but at least they are exact.⁽¹⁻⁵⁾ Twenty-five years or more have elapsed, but the old problems still fascinate. This time, in this paper, we find answers which are exact and have the beauty of simplicity. But they apply only to special cases, and they can be appreciated best only by those workers who have tried their hand at the general theory [which came up again recently in connection with the low-temperature behavior of the quantities (1.1) and (1.2)^(6,7)].

In earlier discussions it does not appear to have been noticed that quite precise comparisons between (1.1) and (1.2) are possible in the special case of a two-state system for which the mean number of indistinguishable particles in the g.c.e. is arranged to be precisely equal to the fixed number N of (indistinguishable) particles in the c.e. As one increases the number of states, the results become more cumbersome and we here restrict attention to two states. That is where the pretty results are

found. Apart from possible applications to quantum wells, these problems have intrinsic interest in showing the relationship between the ensembles in a simple way.

We shall introduce a "pseudo chemical potential" $\mu_j \equiv kT\gamma_j$ for the c.e. by writing (1.2) as

$$n_j(N) = [\exp(n_j - \gamma_j) \pm 1]^{-1}$$

where

$$\exp(-\gamma_j) \equiv Z_{N+1} n_j(N+1) / Z_N n_j(N) \quad (1.3)$$

We need to consider four cases distinguished by appropriate superscripts gF , gB , cF , and cB , where g and c denote g.c.e. and c.e. and F and B denote Fermi and Bose statistics.

2. THEORY OF THE TWO-STATE SYSTEM

Let $E_2 > E_1$ be the energies of the two quantum states, and put

$$a \equiv e^{-\eta_1}, \quad b \equiv e^{\eta_2 - \eta_1}, \quad x \equiv x^{-\gamma}$$

Then the g.c.e. has a value of γ given by

$$n_1(N) + n_2(N) \equiv \frac{1}{x/a \pm 1} + \frac{1}{bx/a \pm 1} = N$$

so that

$$bN \left(\frac{x}{a} \right)^2 \pm (b+1)(N \mp 1) \frac{x}{a} + N \mp 2 = 0 \quad (2.1)$$

where top signs apply to fermions and bottom signs to bosons.

In the case of fermions this equation for x has no acceptable solution except $x=0$ if $N=2$. This means that $n_1(2) = n_2(2) = 1$, as one would expect. If $N=1$, one solves (2.1) for x and finds

$$n_1^{(gF)}(1) = \frac{b^{1/2}}{b^{1/2} + 1}, \quad n_2^{(gF)}(1) = \frac{1}{b^{1/2} + 1}, \quad \frac{n_1^{(gF)}(1)}{n_2^{(gF)}(1)} = b^{1/2} \geq 1 \quad (2.2)$$

In the case of bosons, (2.1) yields

$$n_1^{(gB)}(N) = \left[\frac{(b+1)(N+1)}{2bN} X - 1 \right]^{-1}, \quad n_2^{(gB)}(N) = \left[\frac{(b+1)(N+1)}{2N} X - 1 \right]^{-1} \quad (2.3)$$

where

$$X \equiv 1 \pm \left(1 - \frac{4bN(N+2)}{(b+1)^2(N+1)^2} \right)^{1/2}$$

The top sign has to be chosen in order that $n_1(N) \rightarrow N$, $n_2(N) \rightarrow 0$ as $b \rightarrow \infty$. If $N = 1$, (2.3) yields the relations given in Table I.

Consider next fermions for the c.e. In this case one has

$$Z_0 = 1, \quad Z_1 = e^{-\eta_1} + e^{-\eta_2}, \quad Z_2 = e^{-\eta_1 - \eta_2} \tag{2.4}$$

and one can use

$$n_i(2) = [1 - n_i(1)] Z_1 e^{-\eta_i} / Z_2 \tag{2.5}$$

or

$$n_i(1) = [1 - n_i(0)] Z_0 e^{-\eta_i} / Z_1 \tag{2.6}$$

It is easily seen that (2.4), (2.5), and $n_i(2) = 1$ give the same result as (2.4), (2.6), and $n_i(0) = 0$, namely

$$n_1^{(cF)}(1) = \frac{b}{b+1}, \quad n_2^{(cF)}(1) = \frac{1}{b+1}, \quad \frac{n_1^{(c,F)}(1)}{n_2^{(cF)}(1)} = b \tag{2.7}$$

Comparison of (2.2) and (2.7) shows that

$$\frac{n_1^{(cF)}(1)}{n_2^{(cF)}(1)} = \left[\frac{n_1^{(gF)}(1)}{n_2^{(gF)}(1)} \right]^2 (\geq 1) \tag{2.8}$$

Table I. Details for Equilibrium Systems Containing One Particle^a

Ensemble	Fermions	Bosons
g.c.e.	$n_1^{(gF)}(1) = (b^{-1/2} + 1)^{-1}$ $n_2^{(gF)}(1) = (b^{1/2} + 1)^{-1}$ $\gamma_1 = \gamma_2 = (\eta_2 + \eta_1)/2$	$n_1^{(gB)}(1) = b/[1 + (b^2 - b + 1)^{1/2}]$ $n_2^{(gB)}(1) = 1/[b + (b^2 - b + 1)^{1/2}]$ $\gamma_1 = \gamma_2 = \eta_1 - \ln[1 + b^{-1} + (1 - b^{-1} + b^{-2})^{1/2}]$
c.e.		$n_1^{(cF)}(1) = n_1^{(cB)}(1) = (b^{-1} + 1)^{-1}$ $n_2^{(cF)}(1) = n_2^{(cB)}(1) = (b + 1)^{-1}$ $\gamma_1 = \eta_2, \quad \gamma_2 = \eta_1$

^a $b = \exp(\eta_2 - \eta_1) \geq 1$. For the c.e. the total number of particles is unity. For the g.c.e. the average total number of particles is unity. A chemical potential μ and its reduced version $\gamma = \mu/kT$ exist for the g.c.e.: $\gamma_1 = \gamma_2$. For the c.e. only "pseudo chemical potentials" (1.3) exist and $\gamma_1 \neq \gamma_2$.

Since this ratio is greater than (or equal to) unity,

$$\frac{n_1^{(cF)}(1)}{n_2^{(cF)}(1)} \geq \frac{n_1^{(gF)}(1)}{n_2^{(gF)}(1)}, \quad \text{i.e.,} \quad \begin{cases} n_1^{(cF)}(1) \geq n_1^{(gF)}(1) \\ n_2^{(cF)}(1) \leq n_2^{(gF)}(1) \end{cases} \quad (2.9)$$

Thus, the effect of an energy gap on the population of the levels constituting it is, in the case of fermions, greater for c.e. than it is for the g.c.e.

For the case of bosons in the c.e. use the general result⁽⁵⁾

$$Z_N n(N, j) = \sum_{r=1}^N r S(N; r, j)$$

where $S(N; r, j)$ is the sum of all those terms in Z_N which assign r particles to state j . Now

$$Z_N = \sum_{r=1}^N \exp\{-[r\eta_1 + (N-r)\eta_2]\} = (1 - b^{N+1})/(1 - b) \exp(N\eta_2)$$

and

$$S(N, r, j) = e^{-r\eta_j} e^{-(N-r)\eta_k} = \begin{cases} e^{-N\eta_2} b^r, & j=1 \\ e^{-N\eta_1} b^{-r}, & j=2 \end{cases}$$

Hence,

$$\eta_1^{(cB)}(N) = \frac{(N+1)b^{N+1}}{b^{N+1}-1} - \frac{b}{b-1} \quad (2.10a)$$

$$\eta_2^{(cB)}(N) = \frac{1}{b-1} - \frac{N+1}{b^{N+1}-1} \quad (2.10b)$$

For $N=1$, the relations (2.10) yield the results given in Table I.

It is easy to see that in contrast with (2.9),

$$\begin{aligned} n_1^{(gB)}(1) &\geq n_1^{(B)}(1) \\ n_2^{(gB)}(1) &\leq n_2^{(cB)}(1) \end{aligned} \quad (2.11)$$

The effect of an energy gap on the populations of the levels constituting it is in the case of bosons smaller for the c.e. than it is for g.c.e.

Figure 1 gives the dependence of the occupation numbers of Table I on $\ln b = (E_2 - E_1)/kT$. They all start at $n_1(1) = 1/2$ when the levels are coincident and they all approach $n_1(1) = 1$ as $E_2 - E_1 \rightarrow \infty$. This occurs most rapidly for the gB case and least rapidly for the gF case. The usual exponential decay of the occupation number as the energy level rises can be inferred from Fig. 1 by noticing that $n_2(1) = 1 - n_1(1)$ is represented by the

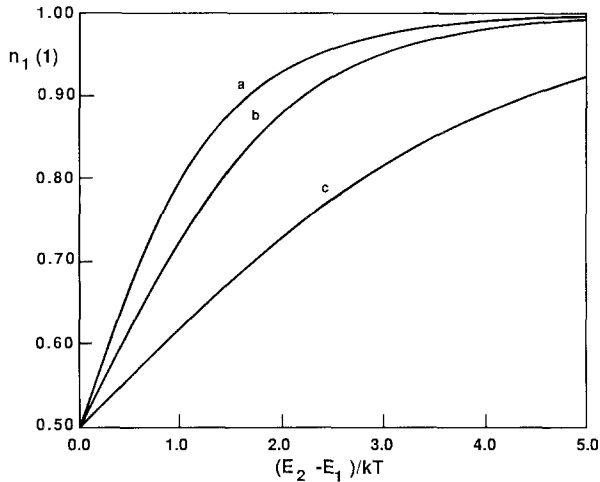


Fig. 1. Mean occupation numbers of the lowest level for a two-state system with one particle. (a) Bosons in the g.c.e. (b) Bosons and fermions in the c.e. (c) Fermions in the g.c.e.

difference between the horizontal line $n_1 = 1$ and the appropriate curve. It is this difference which goes to zero exponentially as $E_2 - E_1 \rightarrow \infty$.

The c.e. does not distinguish between bosons and fermions (curve *b*) because the occupation of the levels cannot bring the Pauli exclusion principle into play. However, for the g.c.e., $N = 1$ is only an average; hence the difference in the statistics is expected to show up (curves *a* and *c*). For bosons, n_1 is highest because of their statistical attraction, leaving a small value for n_2 . For fermions, the statistical repulsion lowers n_1 to curve *c*.

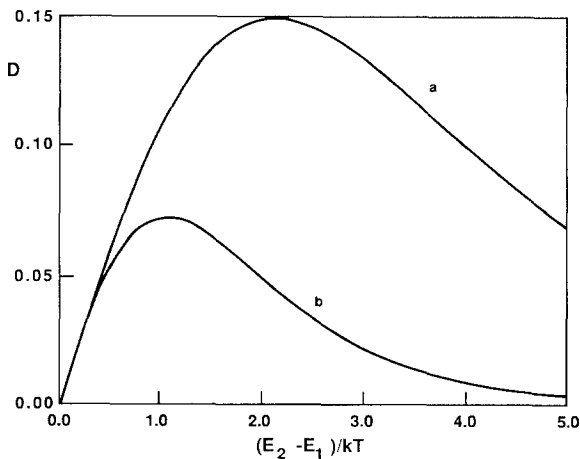


Fig. 2. Ensemble discrepancies for the lowest level for the system of Fig. 1. (a) Fermions. (b) Bosons.

The discrepancies $D^F \equiv n_1^{(cF)}(1) - n_1^{(gF)}(1)$ and $D^B \equiv n_1^{(gB)}(1) - n_1^{(cB)}(1)$ between the ensembles are shown in Fig. 2 and have maxima at

$$(E_2 - E_1)/kT = 2.12 \text{ (fermions)}$$

$$= 1.05 \text{ (bosons)}$$

This corresponds to a maximum discrepancy of

$$\frac{n_1^{(cF)}(1) - n_1^{(gF)}(1)}{n_1^{(cF)}(1)} = 17\%, \quad \frac{n_1^{(gB)}(1) - n_1^{(cB)}(1)}{n_1^{(gB)}(1)} = 9\%$$

For large N the discrepancies between corresponding ensembles are expected to disappear. For example, one finds that both

$$n_1^{(cB)}(N) \text{ and } n_1^{(gB)}(N) \rightarrow N - 1/(b - 1)$$

One can also estimate the entropy

$$S = -k \sum_{i=1}^2 p_i \ln p_i$$

of the four distributions, where k is Boltzmann's constant, and

$$p_i \equiv p_i(N) \equiv n_i(N)/N$$

is the probability for given N of finding a particle in state i . As $E_2 - E_1$ is increased, they drop from the maximum entropy $k \ln 2$ at $E_2 = E_1$ (Fig. 3).

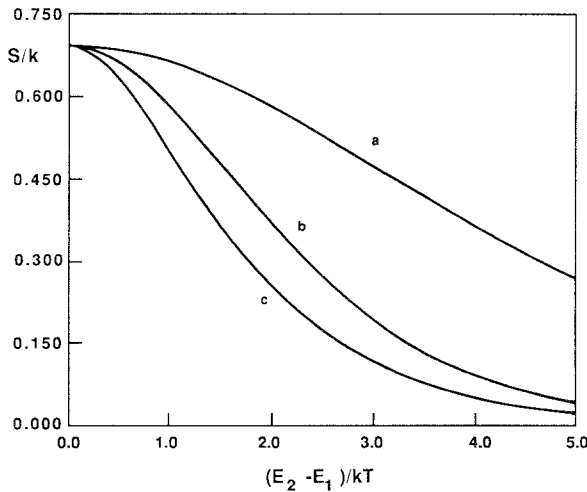


Fig. 3. Entropy for the system of Fig. 1 in units of Boltzmann's constant. (a) Fermions in the g.c.e. (b) Fermions and bosons in the c.e. (c) Bosons in the g.c.e.

3. CONCLUSION

The mean occupation numbers of ideal Fermi and Bose gases have been investigated for canonical and grand canonical ensembles, which are matched by referring to the same temperature, volume, and (mean) number N of particles. The case of two states has been treated in detail. For $N=1$ the canonical ensemble does not distinguish between fermions and bosons and each level has its own "pseudo chemical potential," and these have been identified. The discrepancies between the ensembles have been plotted for $N=1$, when they are most pronounced. As one would expect, they become small for large N .

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