## The fraction of "all different" combinations: Justifying the semi-classical partition function

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Modern statistical mechanics directly acknowledges the indistinguishability of identical particles, a characteristically quantum property. Under laboratory conditions such that classical physics ought to suffice for most purposes, the indistinguishability is often incorporated by a judicious division by N!. This paper explores a common justification for that procedure—and finds it wanting. Nonetheless, the procedure is valid, but for a different reason. © 1997 American Association of Physics Teachers.

Identical particles are indistinguishable, and that quantum property plays a vital role in statistical mechanics. Nonetheless, when a monatomic gas has a temperature and number density like those of air under room conditions, mere division by N! is widely believed to be a sufficient correction to a classical counting of states. In actual fact, the situation is more subtle than that.

The issue arises most clearly when one seeks to evaluate the partition function Z,

$$Z = \sum_{j} \exp(-E_{j}/kT), \qquad (1)$$

for a monatomic ideal gas of N atoms. The sum goes over a complete orthonormal set of energy eigenstates of the entire N-particle system. Each energy  $E_j$  is a sum of single-particle energies,

$$E_{i} = \epsilon_{\alpha}(1) + \epsilon_{\beta}(2) + \dots + \epsilon_{\gamma}(N), \qquad (2)$$

where  $\epsilon_{\alpha}(1)$  denotes the energy of the single-particle state labeled by the subscript  $\alpha$  and where the argument denotes the nominal label of one of the particles.

The key question is whether the "semi-classical" partition function  $Z_{sc}$ , defined by

$$Z_{\rm sc} \equiv \frac{(Z_1)^N}{N!},\tag{3}$$

is a good approximation to Z under realistic physical conditions.<sup>1</sup> The single-particle partition function  $Z_1$  is given by

$$Z_1 = \sum_{\alpha} e^{-\epsilon_{\alpha}(1)/kT}; \tag{4}$$

the sum goes over a complete orthonormal set of singleparticle energy eigenstates.

The numerator in Eq. (3) is a product of sums. Imagine multiplying the factors out, so that the numerator becomes a sum of terms of the form

$$\exp\{-[\epsilon_{\alpha}(1) + \epsilon_{\beta}(2) + \dots + \epsilon_{\gamma}(N)]/kT\}$$
(5)

for some values of the subscripts  $\alpha, \beta, ..., \gamma$ . If all the subscripts are numerically different, the term is acceptable as the Boltzmann factor for an *N*-particle state; it arises in the sum in Eq. (1); and we will call it an "all different" combination of single-particle states. Any such set of subscripts arises *N*! times in the expansion of Eq. (3) but only once in Eq. (1),

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and so the division by N! corrects exactly for the overcounting in the numerator.

If two or more subscripts in Eq. (5) are equal, then the combination is not acceptable for fermions (because of the Pauli exclusion principle); it does not arise in the sum in Eq. (1); and it should be excluded. For bosons, the term is acceptable, but it does not arise as often at N! times in the expansion of  $(Z_1)^N$ . Thus division by N! deprives the term of its proper weight in the sum in Eq. (1).

To be sure, if "most" of the combinations of singleparticle states in  $(Z_1)^N$  are all-different combinations, then  $Z_{sc}$  ought to be a good approximation to Z. No less an authority than Landau and Lifshitz give the impression that such is the case.<sup>2</sup> But is that really so?

Let *n* denote the total number of single-particle states, taken in some practical, meaningful sense. The finiteness of *n* and its behavior as one scales up the system at fixed temperature are the only properties that we need. The single-particle partition function itself gives a good estimate for *n*; the reasoning goes as follows. The exponential in Eq. (4) is essentially 1 for the states with energy up to order kT and is essentially zero for the states with energy much higher than kT. Thus the sum approximates the number of single-particle states that are physically relevant. (The argument is put on firmer, more quantitative ground in Appendix A.) Consequently, let

$$n \cong Z_1 = \frac{V}{h^3} (2\pi m kT)^{3/2}.$$
 (6)

Here, V denotes the container volume, and any multiplicity arising from spin is ignored. Note that n scales as the volume V at fixed temperature. Let me emphasize that Eq. (6) is used only for the scaling of n with V at fixed temperature and for order-of-magnitude estimates. That n is of order  $Z_1$  suffices.

Moreover, the ratio of n to N is readily assessed. Using the estimate in Eq. (6), one has

$$\frac{n}{N} \approx \frac{V}{N} \frac{(2 \pi m k T)^{3/2}}{h^3} \approx 6 \times 10^6,$$
(7)

where the numerical value pertains to air under typical room conditions. The ratio n/N is invariant under scaling at fixed temperature and number density.

To generate an all-different combination in Eq. (5), one can assign numerical values to the subscripts in

$$n(n-1)\cdots(n-[N-1]) \tag{8}$$

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different ways. (The expression includes all permutations of any given set of all-different subscripts.) Altogether—and hence regardless of duplication among some subscripts—one can assign the values in  $n^N$  ways. Thus the fraction of alldifferent combinations, f(n,N), is

$$f(n,N) = 1\left(1-\frac{1}{n}\right)\left(1-\frac{2}{n}\right)\cdots\left(1-\frac{[N-1]}{n}\right).$$
(9)

Is this fraction indeed close to one when  $n/N=6\times10^6$  and  $N=10^{23}$ ?

A good analytic approximation is easily found. Take the logarithm of Eq. (9) and then expand the individual logarithms:

$$\ln f(n,N) = \sum_{q=1}^{N} \ln \left( 1 - \frac{q-1}{n} \right)$$
$$\approx -\sum_{q=1}^{N} \frac{q-1}{n} = -\frac{N(N-1)}{2n}.$$
(10)

Thus

$$f(n,N) \cong \exp\left(-\frac{N^2}{2n}\right). \tag{11}$$

Inserting the values  $n/N=6\times 10^6$  and  $N=10^{23}$ , one finds

$$f \cong \exp(-8 \times 10^{15}). \tag{12}$$

The fraction is embarrassingly small. Almost *none* of the terms in  $(Z_1)^N$  are all-different combinations. Moreover, as Eq. (11) displays, if one scales the system to larger N at fixed N/n, then the fraction becomes even smaller.

How can the semi-classical approximation retain any validity, especially for fermions? Using Eq. (6) to replace  $Z_1$  by *n*, we find from Eq. (3) that

$$Z_{\rm sc} \cong \frac{n^N}{N!} \cong \left(\frac{ne}{N}\right)^N,\tag{13}$$

where the second step uses the dominant part of Stirling's approximation for N!. We can see that  $Z_{sc}$  is an immensely large number. The product of f(n,N) and  $Z_{sc}$  should give a reasonable approximation to the correct partition function for fermions:

$$f(n,N)Z_{\rm sc} \cong \left(e^{-N/2n}\frac{ne}{N}\right)^N.$$
(14)

For most—if not all—calculations in statistical mechanics, the logarithm of the partition function suffices. So consider

$$\ln(fZ_{\rm sc}) \cong N \, \ln\left(e^{-N/2n} \frac{ne}{N}\right). \tag{15}$$

In the argument of the logarithm on the right-hand side, the correction factor has dwindled to virtually 1 and is to be compared with ne/N, which is of order  $10^7$ . Surely, one may ignore the correction factor here.<sup>3</sup>

In short, because  $\ln Z$  or, better yet,  $N^{-1} \ln Z$  play the major role in statistical mechanics, the correction factor has a negligible influence under the physical conditions where a semi-classical analysis ought to be valid. This happy situation arises *despite* the fact that *almost none* of the combinations of single-particles states in  $Z_{sc}$  are legitimate combinations or are properly counted. Once again, the logarithm comes to the rescue.<sup>4</sup>

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Appendix A provides additional mathematical detail and includes the correction factor for bosons. Appendix B gives additional qualitative reasoning: why the correction factor f(n,N) scales with N as it does, and why the factor is so small and hence the correction so large.

What should one tell an undergraduate student about all this? Probably, the less said, the better. Perhaps one remarks that a logarithm is remarkably insensitive to changes in its argument. For example,  $\log(10 \times 10^{100}) \approx \log(10^{100})$ , to within 1 percent. And then one notes that, as an approximation,  $Z_{sc}$  is good enough for all practical purposes.

## APPENDIX A

The quantum distribution functions provide another way to evaluate the correction factor. The estimated occupation numbers are

$$\langle n_{\alpha} \rangle = \frac{1}{e^{(\epsilon_{\alpha} - \mu)/kT} \pm 1},$$
 (A1)

where, here and henceforth, the upper sign applies for fermions and the lower sign, for bosons. The sum of  $\langle n_{\alpha} \rangle$  over all  $\alpha$  must equal N, a constraint that determines the chemical potential  $\mu$ . In broad outline, the procedure is this: First use Eq. (A1) to get the chemical potential; then use  $\mu$  in a recursion relation for the partition function, iterating the relation from Z(N) downward to the known Z(1), where the argument indicates the number of gas atoms in the system.

When the physical system behaves nearly like a classical gas, the exponential in Eq. (A1) must be much larger than  $|\pm 1|$  for all  $\alpha$ , so that the distinction between fermions and bosons is relatively insignificant. One can expand  $\langle n_{\alpha} \rangle$  through its first correction term beyond the classical term and impose the constraint that determines the chemical potential:

$$e^{\mu/kT} \sum_{\alpha} e^{-\epsilon_{\alpha}/kT} + e^{2\mu/kT} \sum_{\alpha} e^{-2\epsilon_{\alpha}/kT} = N.$$
 (A2)

The first sum is simply  $Z_1$ . Equation (6) showed that  $Z_1$  is proportional to  $T^{3/2}$ . For the second sum, think of it as like the first sum but with T/2 in place of T. That view implies that the second sum equals  $2^{-3/2}Z_1$ . Solving Eq. (A2) for  $\exp(\mu/kT)$ , one finds

$$e^{\mu/kT} = \frac{N}{Z_1} \left( 1 \pm \frac{1}{2^{3/2}} \frac{N}{Z_1} + \cdots \right) \cong \frac{N}{Z_1} \exp\left( \pm \frac{1}{2^{3/2}} \frac{N}{Z_1} \right),$$
(A3)

provided  $N/Z_1 \ll 1$ . (Additional steps in the algebra are displayed in Ref. 1, pp. 303–305.)

A recursion relation,

$$Z(N) = e^{-\mu/kT} Z(N-1),$$
(A4)

follows from the definition of the chemical potential as the change in the Helmholtz free energy [which can be written as  $-kT \ln Z(N)$ ] when one atom is added to the system. For the factor  $\exp(-\mu/kT)$ , use the reciprocal of Eq. (A3) and iterate the recursion relation downward:

$$Z(N) \cong Z(1) \prod_{j=2}^{N} \frac{Z_1}{j} \exp\left( \mp \frac{1}{2^{3/2}} \frac{j}{Z_1} \right)$$
$$= \frac{(Z_1)^N}{N!} \exp\left( \mp \frac{1}{2^{3/2} Z_1} \sum_{j=2}^{N} j \right).$$
(A5)

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Because the sum over j equals  $N^2/2$  (plus insignificant terms), the outcome is

$$Z(N) \approx \frac{(Z_1)^N}{N!} \exp\left(\mp \frac{N^2}{2} \frac{1}{2^{3/2} Z_1}\right).$$
 (A6)

The correspondence between the estimate in Eq. (11) and this result is excellent. The equivalent "total number" of single-particle states is  $n=2^{3/2}Z_1$ .

For bosons, the correction factor is greater than one and compensates for the *under* counting in  $Z_{sc}$  of *N*-particle states with multiple occupancy of single-particle states.

## **APPENDIX B**

Why does the correction factor f(n,N) scale with N as it does, and why is it so small? Let us remain with fermions. The product  $(Z_1)^N/N!$  certainly contains some terms that have repeated subscripts on the energy expression and hence do not belong in a partition function for fermions. Consequently, there must be a correction factor (smaller than 1). The factor may depend on the extensive variable N and the intensive variable N/n. Because  $-kT \ln Z$  gives the Helmholtz free energy, which is extensive and proportional to N, the correction factor must have the form

$$f(n,N) = [g(N/n)]^N \tag{B1}$$

for some function g(N/n). Because N/n is of order  $10^{-7}$  under typical room conditions, the function g(N/n) ought to be less than one by only a modest amount. Nonetheless, when g(N/n) is raised to the power  $N=10^{23}$ , the result may be tiny indeed.

The structure in Eq. (B1) suggests a graphic illustration of the formal calculation in Eqs. 8-11. Imagine the integers 1

to *n* written in a tall column. Further, imagine *N* such columns, arranged left to right. You are to pick a number—at random—from each column, starting with the column on the left end. When you reach the middle, you will have picked N/2 numbers. Suppose, they are all different. Then the probability that your next random choice (in the next column) will be one of those numbers is (N/2)/n and is small. The probability of your choosing a number *not* already picked is  $1 - N/2n \cong \exp(-N/2n)$  and is very close to unity.

Now adopt  $\exp(-N/2n)$  as the "average" probability of choosing a number not already picked. The probability of *never* duplicating is then the *N*-fold product of  $\exp(-N/2n)$ , at least approximately. The ensuing product has the structure of Eq. (B1), reproduces Eq. (11), and is remarkably small. In short, it is hard to achieve a perfect record.

<sup>1</sup>Ralph Baierlein, *Atoms and Information Theory* (Freeman, New York, 1971), pp. 307–308.

<sup>2</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1958), pp. 119–120, especially the second footnote on p. 120.

<sup>3</sup>Calculations of the correction date from at least 1932: G. E. Uhlenbeck and L. Gropper, "The equation of state of a non-ideal Einstein–Bose or Fermi–Dirac gas," Phys. Rev. **41**, 79–90 (1932). Other pertinent papers are D. I. Ford, "A note on the partition function for systems of independent particles," Am. J. Phys. **39**, 215–220; A. G. McLellan, "The classical limit of the partition function in statistical mechanics," *ibid.* **40**, 704– 709 (1972); H. Kroemer, "How incorrect is the classical partition function for the ideal gas?," *ibid.* **48**, 962–963 (1980); F. Hynne, "Quantum statistics of an ideal molecular gas," *ibid.* **49**, 125–127 (1981); F. Hynne, "The population structure of an ideal boson gas," *ibid.* **50**, 806–807 (1982); and R. L. Ingraham, "When can we treat identical particles as distinguishable? An unfamiliar classical limit," *ibid.* **53**, 119–122 (1985). The present paper is intended to complement those earlier treatments.

<sup>4</sup>R. H. Romer, "Editorial: Strong inequalities II—Logarithms," Am. J. Phys. **64**, 111–112 (1996).