

# Fermi-Dirac Statistics

Simon Saunders

**Fermi-Dirac statistics** are one of two kinds of statistics exhibited by  $\rightarrow$ identical quantum particles, the other being  $\rightarrow$ *Bose-Einstein statistics*. Such particles are called *fermions* and *bosons* respectively (the terminology is due to Dirac [1902-1984] [1]). In the light of the  $\rightarrow$ spin-statistics theorem, and consistent with observation, fermions are invariably spinors (of half-integral spin), whilst bosons are invariably scalar or vector particles (of integral spin). See  $\rightarrow$ spin.

In general, in quantum mechanics, the available states of a homogeneous many-particle system in thermal equilibrium, for given total energy, are counted as *equiprobable*. For systems of *exactly similar* ('identical') fermions or bosons, states which differ only in the permutation of two or more particles are not only counted as equiprobable – they are *identified* (call this *permutivity*). Fermions differ from bosons in that no two fermions can be in exactly the same 1-particle state. This further restriction follows from the  $\rightarrow$ *Pauli exclusion principle*. The thermodynamic properties of gases of such particles were first worked out by Fermi [1901-1954] in 1925 [2], and, independently, by Dirac in 1926 [3].

To understand the consequences of these two restrictions, consider a system of  $N$  weakly-interacting identical particles, with states given by the various 1-particle energies  $\epsilon_s$  together with their degeneracies – the number  $C_s$  of distinct 1-particle states of each energy  $\epsilon_s$ . From permutivity, the total state of a gas is fully specified by giving the number of particles with energy  $\epsilon_s$  in each of the  $C_s$  possible states, i.e. by giving the *occupation numbers*  $n_k^s$  for each  $s$ ,  $k = 0, 1, \dots, C_s$ . We suppose all possible states of the same total energy  $E$  and, supposing particle number is conserved, of the same total number  $N$ , are available to the  $N$  particles when in thermal equilibrium, i.e. all sets of occupation numbers that satisfy:

$$\sum_{s,k=1}^{k=C_s} n_k^s = \sum_s N_s = N; \quad \sum_s N_s \epsilon_s = E. \quad (1)$$

Since this is quantum mechanics, we suppose that superpositions of such states are available to the system as well.

Imposing Pauli's restriction that no two particles can be in the same 1-particle state, it follows that the occupation numbers are all zeros and ones and that  $C_s \geq N_s$ . The number of distinct sets of occupation numbers  $n_0^s, n_1^s, \dots, n_{C_s}^s$  that sum to  $N_s$  satisfying this condition is:

$$\frac{C_s!}{N_s!(C_s - N_s)!}$$

Since the occupation number states span the subspace of the total  $\rightarrow$ Hilbert space to which the  $N_s$  particles are confined, this is the dimensionality – the 'volume' – of the available spate space for fermions of energy  $s$ .

For comparison, if the exclusion principle is not obeyed, the number of distinct sets of  $\{n_k^s\}$  that sum to  $N_s$  is rather:

$$\frac{(C_s + N_s - 1)!}{N_s!(C_s - 1)!}$$

the state-space measure that applies to bosons of energy  $s$ . The total number of distinct sets of occupation numbers for  $N = \sum_s N_s$  particles is then for fermions:

$$P_- = \prod_s \frac{C_s!}{N_s!(C_s - N_s)!}$$

and for bosons:

$$P_+ = \prod_s \frac{(C_s + N_s - 1)!}{N_s!(C_s - 1)!}.$$

By conventional reasoning, the equilibrium coarse-grained distribution is that for which  $P_{\pm}$  is a maximum. The equilibrium entropy is proportional to the logarithm of this number,  $S_{\pm} = k \log P_{\pm}$ , where  $k$  is Boltzmann's constant. Using the Stirling approximation for  $x \gg 1$ ,  $\log x! \approx x \log x - x$ , the two entropy functions are:

$$S_{\pm} = k \log P_{\pm} \approx k \sum_s [\mp C_s \log C_s - N_s \log N_s - (\mp C_s - N_s) \log(C_s \pm N_s)].$$

If this is to be stationary under independent variation of the numbers  $N_s \rightarrow N_s + \delta N_s$ , subject to the constraints (1), then

$$0 = \delta \log P_{\pm} = \sum_s [-\delta N_s \log N_s + \delta N_s \log(C_s \pm N_s)].$$

Were the variations  $\delta N_s$  completely independent each term in this summand would have to vanish. Introducing undetermined Lagrange multipliers  $\alpha$ ,  $\beta$ , for each of the constraints (1), conclude rather that for each  $s$ :

$$-\log N_s + \log(C_s \pm N_s) - \alpha - \beta \epsilon_s = 0.$$

Rearranging:

$$N_s = C_s (e^{\alpha + \beta \epsilon_s} \mp 1)^{-1}. \quad (2)$$

In the case of light quanta, there is no constraint on particle number and the multiplier  $\alpha$  does not occur. The multiplier  $\beta$  meanwhile has its usual meaning,  $\beta = 1/kT$ , where  $T$  is the absolute temperature.  $C_s$  is the number of distinct 1-quanta states in the energy range  $[\epsilon_s, \epsilon_s + d\epsilon_s]$ , where  $\epsilon_s = h\nu_s$ . It is given by:

$$C_s = 8\pi V \nu_s^2 d\nu_s / c^3 \quad (3)$$

(obtained either classically, from the wave theory, or by Bose's method). From (2) and (3) the Planck black-body radiation law follows immediately. The numbers  $N_s$  of (2) are proportional to the radiation energy density in the frequency range  $[\nu_s, \nu_s + d\nu_s]$ , which can be directly measured.

The contrast with the statistics of non-identical particles is that in the latter case (failing permutivity) there is the further question of which of the  $N_s$  particles is in which of the  $C_s$  one-particle states ( $C_s^{N_s}$  possible distributions in all). There is also the question of how the  $N$  particles are partitioned into the occupation numbers  $N_1, N_2, \dots, N_s, \dots$ . Taking both into account, the total number of distinct states  $P_0$  with occupation numbers  $N_1, \dots, N_s, \dots$  is:

$$\frac{N!}{N_1! \dots N_s! \dots} \prod_s C_s^{N_s}. \quad (4)$$

By a similar calculation as before, this yields:

$$N_s = C_s e^{-\alpha - \beta \epsilon_s} \quad (5)$$

Evidently (2) (for either sign) and (5) are approximately the same for  $C_s \gg N_s$  (equivalently, when  $\alpha + \beta \epsilon_s \gg 1$ ), and the difference in the statistics for identical and non-identical particles disappears.

At the other extreme, for bosons for which  $C_s \ll N_s$ , from (2) it follows:

$$N_s = C_s (\alpha + \beta \epsilon_s)^{-1}. \quad (6)$$

For  $\alpha = 0$ , and  $C_s$  as given by (3), (6) is the *Rayleigh-Jeans black-body distribution*; (5) is the *Wien distribution*. The discovery of Planck's constant began with the puzzle of how to understand these distributions, which yielded the observed long ( $C_s \ll N_s$ ) and short ( $C_s \gg N_s$ ) wavelength behaviour respectively, and with Planck's black body formula (2) (with negative sign), obtained by interpolating between them [10]. The method of counting (4) is associated with *Maxwell-Boltzmann* or *classical* statistics. It was derived, using specifically quantum-mechanical methods, by Ehrenfest [1880-1933] and Uhlenbeck [1900-1988] immediately after the discovery of Fermi's statistics. They concluded that 'wave mechanics does not yet *per se* imply the refutation of Boltzmann's method' [4 p.24]. The difference, in quantum mechanics, resides *solely* in the assumption of permutivity. It is an easy slide to think, since classical statistical mechanics delivers the same statistics as quantum mechanics for non-identical particles, that classical particles likewise are non-identical (and do not satisfy permutivity), i.e. that the *correct* classical count of states  $P_0$  is (4). But Gibbs [1839-1903] had argued for the permutivity of classical particles long before [6], and for a non-quantized classical phase space, permutivity makes no difference to the statistics [11]. That is, computing the *volume* of classical phase space, subject to permutivity, rather than a count of equiprobable states, one should use:

$$P_0 = \prod_s \frac{C_s^{N_s}}{N_s!} \quad (7)$$

rather than (4). The logarithm of  $P_0$  as given by (7) yields an extensive entropy function, as required [12].

Fermi in 1924 was led to assume that no two electrons could occupy the same elementary volume in phase space, because only thereby could he obtain

agreement with the Sarkur-Stern expressions for the chemical potential and absolute entropy [5]. That was enough, the following year, to get out a new equation of state, but little more. Dirac, a few months later, had many more fragments of the nascent theory of quantum mechanics to hand. He considered the question of how to formulate permutivity in terms of matrix mechanics directly. He was led to the question by Heisenberg's dictum: the new mechanics was to be restricted to *observable* quantities. In matrix mechanics the observable quantities were the matrix elements, corresponding to the intensities of the various transition processes giving rise to line spectra. In the still unresolved problem of the helium atom, the question arose of how to treat a transition involving both electrons in one-particle states  $\psi_n, \psi_m$ , of the form  $(mn) \rightarrow (m'n')$ , and its relation to the transition  $(mn) \rightarrow (n'm')$ . Only the sum of the two, Dirac noted, was observable. 'Hence, in order to keep the essential characteristic of the theory that it shall enable one to calculate only observable quantities, one must adopt the second alternative that  $(mn)$  and  $(nm)$  count as only one state.' [3 p.667].

Incorporating this into the matrix mechanics (and in particular in terms of his theory of uniformizing variables) presented certain technical difficulties, whereas in wave mechanics the way forward was much easier (an early indicator for Dirac that Schrodinger's wave theory may have definite advantages over the matrix mechanics). In the two particle case the state  $(mn)$  of the composite system of electrons, labelled 1 and 2, must be of the form

$$\psi_{mn} = a_{mn}\psi_m(1)\psi_n(2) + b_{mn}\psi_n(1)\psi_m(2) \quad (7)$$

where  $a_{nm} = \pm b_{nm}$  (and superpositions of such). Dirac observed that the antisymmetric case ( $a_{nm} = -b_{nm}$ ) leads to Pauli's principle and the symmetric case to the Bose-Einstein statistical mechanics. He went on to deduce the theory just sketched; he thought, as had Fermi, that the new statistics, applying as it did to electrons in the atom, was likely to apply to material gases as well.

Dirac shortly after remarked on the possibility of alternative ('more complicated') representations of the permutation group, other than the completely symmetrized (boson) and antisymmetrized (fermion) representations (in 1930, in the first edition of his *Principles*). These alternatives lead to a variety of different statistics - *parastatistics* - that are not realized in nature (or not in 3+1 dimensions; special considerations apply to particles effectively restricted to two spatial dimensions). It was thought, for a time, that they might offer an alternative to the quark model of deep inelastic scattering, but without success [13].

Heisenberg [1901-1976] as well as Dirac had been preoccupied with the helium problem. His earlier papers in 1926 on the helium and related 2-electron spectra had made use of the Pauli exclusion principle and, for the first time, the Schrödinger wave mechanics (albeit only as a calculational tool). He too arrived at the two classes of states (7), but under a somewhat different interpretation from Dirac's and with no understanding of the fact that they gave rise to different statistics. He was led, rather, to an idea absent from Dirac's paper - that

a two-electron system, each with identical allowed energies  $E_m(1) = E_m(2)$ ,  $E_n(1) = E_n(2)$  (with  $E_n > E_m$ ), would in wave-theoretic terms be subject to *resonance*, with energy  $E_n - E_m$  passing from one electron to the other under the transition  $(mn) \rightarrow (nm)$  (states that Dirac had *identified*). Likewise the perturbation due to the electron charge ‘will in general contain terms corresponding to transitions in which the systems 1 and 2 switch places (‘den Platz tauschen’) [7 p.417].

Thus did the idea of *exchange forces* first arise. A similar interpretation was advanced by Heitler [1904-1981] and London [1900-1954] the following year in their treatment of the homopolar bond [8]. But by this time, as Heitler went on to remark, this question of interpretation had become closely wed to disputes over other interpretative issues in quantum mechanics, notably over Schrödinger’s continuous beat picture of emission and absorption processes as compared to Born’s statistical interpretation [14]. What was being exchanged, Heitler concluded, ‘remained completely unclear.’ ([9 p.48]).

What *was* clear was that in any of the symmetric, triplet states of spin, for which the spatial wave-function must be antisymmetric, the norm of the wave-function for electron coordinates close together is extremely small (and for coinciding coordinates, vanishes). In this sense electrons in bound states with correlated spins effectively repel one another. Those with anticorrelated spins, in the antisymmetric singlet state, have greater amplitudes for small relative distances, for their spatial wavefunction must then be symmetric - the amplitude is much greater than if there were no overall symmetry requirement on the state (the case of non-identical fermions). This effect is independent of the Coulomb force altogether, and plays a key role in ferromagnetism as well in the chemical bond, as Heisenberg was shortly to show, again with reference to ‘electron exchange’, and ‘exchange forces’.

Whether interpreted as an exchange force involving the  $\rightarrow$ -identity of quantum particles over time, or as a consequence of permutivity and the Pauli exclusion principle, Fermi-Dirac statistics is fundamental to the whole of quantum chemistry and throughout the physics of the solid state.

## Literature

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