Additional material

An introduction the Atomic and Radiation Physics of Plasmas

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1 Introduction

Additional material related to the development of particle distribution functions for 'Tallents, G. (2018). An Introduction to the Atomic and Radiation Physics of Plasmas. Cambridge: Cambridge University Press' is presented here. The text of the book develops the physics of emission, absorption and interaction of light in astrophysics and in laboratory plasmas from first principles using the physics of various fields of study including quantum mechanics, electricity and magnetism, and statistical physics. This text can be regarded as an additional Appendix to the book. References to Equations and Sections given with decimal numbering refer to those presented in the book.

2 The Boltzmann and Fermi-Dirac distributions

In Section 8.1 we show that particles can be designated as fermions, where only a maximum of one particle can occupy a quantum state, or as bosons where any number of particles can occupy a quantum state. In a book on atomic and radiation physics, we are mainly concerned with electron quantum states (representing fermions) or the quantum states associated with photons (representing bosons).

The probability P(E) of finding a particle in a quantum state of energy Eat a temperature T is given by Equation 1.19. By including the number N of particles allowed to occupy the quantum state of energy E, Equation 1.19 enables a presentation in the same expression of the probability of having either fermions or bosons in a quantum state. The Pauli exclusion principle (see section 8.1) allows fermions to have either N = 0 or N = 1 particles in the same quantum state, while bosons can have have N = 0, 1, 2, ... (up to any integer). Equation 1.19 is given as a probability proportionality:

$$P(E) \propto \exp\left(\frac{N(\mu - E)}{k_B T}\right)$$

where μ is the chemical potential. The chemical potential is the energy per particle required to add more particles into the available quantum states.

Equation 1.19 is used to determine the Maxwellian distribution of speeds in Section 1.2 and then to derive the Saha-Boltzmann ratio of the populations of different ionisation stages at low density in Section 1.4.1. In later chapters, the probability of having a particle in a quantum state is employed in the derivation of the Planck black-body radiation distribution, enabling a calculation of the probability of the number of photons in a mode (Section 4.1.2). Finally, the Boltzmann ratio of populations is utilised to derive the high density form of the Saha-Boltzmann equation (Section 13.4).

To derive Equation 1.19, we need to consider the change ΔU of the total energy U of an assumed large number n_{tot} of particles distributed into a number of quantum states. From equilibrium thermodynamics, we have for a constant temperature T and constant chemical potential μ that any change in the total energy U of a collection of quantum states arises from a change in the entropy Splus any energy change due to the addition of Δn_{tot} more particles. We have

$$\Delta U = T\Delta S + \mu \Delta n_{tot}.$$
 (1)

In thermodynamics, entropy change ΔS is defined by the first term on the right in Equation 1. There is additional energy associated with an increase in the 'disorder' represented by the entropy.

The total energy U is determined by adding up the energy of each quantum state multiplied by the number of particles in the state, so that

$$U = \sum_{i} N_i n_i E_i \tag{2}$$

where N_i is the number of particles allowed in the *i*th quantum state and n_i is the number of quantum states in the system with an energy E_i . We discussed previously that for fermions, N_i is either zero or one, where for bosons N_i can range from 0, 1, 2, ... up to any integer. So as not violate the Pauli exclusion principle, we are assuming that the different quantum states with the same energy are separated into different atoms (for bound electrons) or satisfy the possible density of quantum states (for free electrons, see section 1.3).

The total number of particles is determined from a summation of the particle number over all the quantum states. We have

$$n_{tot} = \sum_{i} N_i n_i. \tag{3}$$

In statistical physics, the entropy S of a system is determined by the number of ways Q that particles can be arranged in the collection of quantum states of the system. We have that

$$S = k_B \ln Q. \tag{4}$$

We show below that this definition of entropy is consistent with the thermodynamic definition stated in terms of the change ΔU of total energy of the particles due to increasing entropy ΔS :

$$\Delta S = \frac{\Delta U}{T}.$$

The logarithm in Equation 4 is useful in obtaining an approximate value for the entropy. Fortunately, the approximation we will use becomes very accurate when the number n_{tot} of particles is large. The number of distinct arrangements of n_{tot} indistinguishable particles into quantum states (which we are labelling as *i*) is given by probability theory. We have that the number of distinct arrangements Qis given by the factorial of the total number n_{tot} of particles divided by the product of factorials of the number n_i of particles in each quantum state *i* of the system¹:

$$Q = \frac{n_{tot}!}{\prod_i n_i!}.$$
(5)

The total number of ways that n_{tot} particles can be arranged is n_{tot} !. We are not concerned with the order of 'placing' the particles in each of the quantum states *i* as we assume that they are indistinguishable, so Equation 5 divides the total number of arrangements by the number of ways n_i ! that n_i particles can be arranged in each quantum state *i*. This is done for each quantum state *i* giving rise to the product in the denominator.

Taking the logarithm of Q gives

$$\ln Q = \ln(n_{tot}!) - \sum_{i} \ln n_{i}.$$

The Stirling approximation is a convenient simplification for the factorial of n_{tot} . For large x, we have

$$\ln(x!) \approx x \ln x - x.$$

¹Equation 5 assumes that particles have sufficient time and sufficient interaction for all the quantum states to be accessible. For fermions, collisions between particles often ensure equal accessibility, leading to equilibrium distributions where, for example, Equation 1.19 is valid. For photons and other bosons, the particles need to interact with electrons (or other fermions).

The value of $\ln Q$ becomes

$$\ln Q = n_{tot} \ln n_{tot} - n_{tot} - \sum_{i} n_{i} \ln n_{i} + \sum_{i} n_{i}.$$
 (6)

Returning to the energy balance equation (Equation 1), we can divide throughout by a small increment Δn_j of the population of n_j quantum states associated with a quantum state j. Taking the limits of small increments and using $S = k_B \ln Q$, we have a differential equation

$$\frac{\partial U}{\partial n_j} = k_b T \frac{\partial \ln Q}{\partial n_j} + \mu \frac{\partial n_{tot}}{\partial n_j}.$$
(7)

Each of these terms simplifies considerably. Using the summation of all quantum state energies given by Equation 2 we have

$$\frac{\partial U}{\partial n_j} = N_j E_j. \tag{8}$$

All values in the summation of U are zero in the partial derivative except when i = j. Similarly, using Equation 3 we have that

$$\mu \frac{\partial n_{tot}}{\partial n_j} = N_j \mu$$

The partial derivative of $\ln Q$ also simplifies. We can differentiate $\ln Q$ using Equation 6. The total number of particles n_{tot} is constant when considering the partial derivative with respect to the population of the *j*th quantum state and again the summations are only non-zero upon partial differentiation when i = j. We have

$$\frac{\partial \ln Q}{\partial n_j} = -\ln n_j. \tag{9}$$

The result of these simplifications is

$$N_j E_j = -k_B T \ln n_j + \mu N_j.$$

Re-arranging gives

$$n_j = \exp\left(\frac{N_j(\mu - E_j)}{k_B T}\right). \tag{10}$$

Dropping the sub-script j, we then have a probability for the occupation of a quantum state of energy E determined by

$$P(E) = \exp\left(\frac{N(\mu - E)}{k_B T}\right) / n_{tot}.$$
(11)

2.0.1 Fermion and bosons

For fermions, the average occupancy n(E) of a quantum state with energy E is determined by the ratio of the probability of occupation when a particle can be present in the quantum state (N = 1) to the addition of the two probabilities when a further occupancy is not allowed (N = 0) and allowed (N = 1). We obtain Equation 1.20 with

$$n(E) = \frac{P(N=0)}{P(N=1) + P(N=0)} = \frac{\exp((\mu - E)/k_B T)}{\exp((\mu - E)/k_B T) + 1} = \frac{1}{1 + \exp((-\mu + E)/k_B T)}$$

We may have several quantum states with the same energy E or an energy within a small range E to E+dE. Equation 11 shows for fermions that if the energy E is the same for different quantum states then the probability P(E) of occupation is the same. We can allow for the effect on the populations of different quantum states with the same energy by multiplying the average occupancy by a 'degeneracy' g(also known as a statistical weight) which is the number of distinct quantum states with the same energy. If the degeneracy or density of states in the energy range Eto E + dE is g(E), the population of all quantum states with energy E to E + dEis given by

$$f_{FD}(E)dE = \frac{g(E)dE}{1 + \exp((-\mu + E)/k_BT)}$$
(12)

where g(E) is the degeneracy or density of quantum states at energy E. This distribution is known as the Fermi-Dirac distribution. It is used in Section 13.3.

The chemical potential μ for a collection of electrons is obtained by integrating Equation 12 over all energy and equating this integrated value to the known number of electrons in the system. Usually the number of electrons per unit volume, that is the electron density n_e is known. The degeneracy g(E) is then specified as the number of quantum states per unit energy per unit volume. In dealing with a bound quantum state, the electron degeneracy is specified as the number of quantum states with the same energy per atom or ion.

At low densities and high temperatures, the chemical potential μ is large and negative (see Section 13.3), so that the population of quantum states are proportional to $g(E) \exp(-E/k_B T)$. The ratio of two discrete quantum state populations n per unit volume which we label for the higher energy state with subscript 'u' and for the lower energy state with subscript 'l' is given by Equation 1.27 and is known as the Boltzmann ratio. Equation 1.27 is written as:

$$\frac{n_u}{n_l} = \frac{g_u}{g_l} \exp\left(-\frac{\Delta E}{k_B T}\right)$$

where the energy difference of the two quantum states is ΔE and g_u and g_l are respectively the upper and lower quantum state degeneracies.

In Section 4.1.2, we determined the Planck black body radiation distribution. Part of this calculation involved evaluating the probability of the presence of n_p photons with energy $\hbar \omega$ for a radiation temperature of T. As photons are bosons, the chemical potential is zero. Adding a boson to a collection of bosons does not release or require any energy. In addition, the parameter N in Equation 11 can represent any number of photons in the same mode. The probability of having n_p photons per mode can be regarded as following Equation 11 so that

$$P_{n_p} = \frac{\exp(-n_p \hbar \omega / k_B T)}{\sum_{n'} \exp(-n' \hbar \omega / k_B T)}$$

where the summation in the denominator is from n' = 0 up to $n' = \infty$. The average number of photons n_{av} per mode is then given by

$$n_{av} = \sum_{n_p} n_p P_{n_p} = \frac{1}{\exp(\hbar\omega/k_B T) - 1}.$$

The expression on the right hand side is derived in Section 4.1.2. This value of n_{av} can be generalised to represent the average occupancy of bosons in a quantum state of energy E after replacing $\hbar \omega$ by E. There is a superficial resemblance to the average occupancy of fermions (given by Equation 1.20), except the minus in the denominator for bosons becomes a plus for fermions.

2.0.2 The thermodynamic and statistical physics entropy

The thermodynamic definition of an entropy change ΔS defines entropy in terms of the change of total energy ΔU by specifying that $\Delta S = \Delta U/T$. This definition assumes that the chemical potential remains constant and the temperature remains constant. The statistical physics definition is given by Equation 4 with $S = k_B \ln Q$. We need to show that the two definitions are consistent.

With constant chemical potential μ and constant temperature T, we can have an increase in entropy S associated with an increase of the total energy U by adding the entropy increase due to an increase in 'disorder' (represented by $k_B \ln Q$) and the increase in entropy associated with the addition of particles. We have (see Equation 1) that the additional energy associated with an increase of the total particle number n_{tot} is given by $\mu \Delta n_{tot}$. The increase of entropy associated with the increase of particle number is consequently $(\mu/T)\Delta n_{tot}$. Adding the differential of the entropy increase due to disorder plus the entropy increase due to particle number with respect to the total energy U gives

$$\frac{dS}{dU} = \frac{\partial(k_B \ln Q)}{\partial U} + \frac{\mu}{T} \frac{\partial n_{tot}}{\partial U}.$$

We can write for any of the quantum states j that

$$\frac{\partial \ln Q}{\partial U} = \frac{\partial \ln Q}{\partial n_j} \frac{\partial n_j}{\partial U} = (-\ln n_j) \frac{1}{N_j E_j}$$

upon using Equation 9 for the differentiation of $\ln Q$ and Equation 8 for the differentiation of the total energy U. For the term involving the chemical potential μ , we write that

$$(\mu/T)\frac{\partial n_{tot}}{\partial U} = (\mu/T)\frac{\partial n_{tot}}{\partial n_j}\frac{\partial n_j}{\partial U} = \frac{\mu/T}{E_j}.$$

Using the Boltzmann factor for n_j with $n_j = \exp(N_j(\mu - E_j)/k_BT)$ gives the required result that

$$\frac{dS}{dU} = \frac{\partial(k_B \ln Q)}{\partial U} + \frac{\mu}{T} \frac{\partial n_{tot}}{\partial U} = (-\ln n_j) \frac{k_B}{N_j E_j} + \frac{\mu/T}{E_j} = \frac{1}{T}$$