8.4: Boltzmann's Equation

If we have a large number of atoms in a hot, dense gas, the atoms will constantly be experiencing collisions with each other, leading to excitation to the various possible energy levels. Collisional excitation will be followed, typically on timescales of the order of nanoseconds, by radiative deexcitation. If the temperature and pressure remain constant, there will exist a sort of dynamic equilibrium between collisional excitations and radiative de-excitations, leading to a certain distribution of the atoms among their various energy levels. Most of the atoms will be in low-lying levels; the number of atoms in higher levels will decrease exponentially with energy level. The lower the temperature, the faster will be the population drop at the higher levels. Only at very high temperatures will high-lying energy levels be occupied by an appreciable number of atoms. Boltzmann's Equation shows just what the distribution of the atoms will be among the various energy levels as a function of energy and temperature.

Let's imagine a box (constant volume) holding N atoms, each of which has m possible energy levels. Suppose that there are N_j atoms in energy level E_j. The total number N of atoms is given by

$$N=\sum_{i=1}^{m} N_i. \tag{8.4.1}$$

Here, i is a running integer going from 1 to m, including j as one of them.

The total internal energy U of the system is

$$U=\sum_{i=1}^{m} N_i E_i. \tag{8.4.2}$$

We now need to establish how many ways there are of arranging N atoms such that there are N_1 in the first energy level, N_2 in the second, and so on. We shall denote this number by X. To some, it will be intuitive that

$$X=\frac{N!}{N_1!N_2!\ldots\ldots N_j!\ldots\ldots N_m!}. \tag{8.4.3}$$

That is,

$$X=\frac{N!}{\prod_{i=1}^{m} N_i!}. \tag{8.4.4}$$

I don't find it immediately obvious myself, and I am happier with at least a minimal proof. Thus, the number of ways in which N_1 atoms can be chosen from N to occupy the first level is $\binom{N}{N_1}$, where the parentheses denote the usual binomial coefficient. For each of these ways, we need to know the number of ways in which N_2 atoms can be chosen from the remaining $N-N_1$. This is, of course, $\binom{N-N_1}{N_2}$. Thus the number of ways of populating the first two levels is $\binom{N}{N_1}\binom{N-N_1}{N_2}$.

On continuing with this argument, we eventually arrive at

$$X=\binom{N}{N_1}\binom{N-N_1}{N_2}\binom{N-N_1-N_2}{N_3}\ldots\ldots\binom{N-\sum_1^{m-1} N_i}{N_m}. \tag{8.4.5}$$

If the binomial coefficients are written out in full (do it - don't just take my word for it), there will be lots of cancellations and you almost immediately arrive at Equation 8.4.3.

We now need to know the most probable partition - i.e. the most probable numbers N_1, N_2, etc. The most probable partition is the one that maximizes X with respect to *each* of the N_j - subject to the constraints represented by Equations 8.4.1 and 8.4.2.

Mathematically it is easier to maximize $\ln X$, which amounts to the same thing. Taking the logarithm of Equation 8.4.3, we obtain

$$\ln X=\ln N!-\ln N_1!-\ln N_2!-\ldots \tag{8.4.6}$$

Apply Stirling's approximation to the factorials of all the variables. (You'll see in a moment that it won't matter whether or not you also apply it to the constant term $\ln N!$) We obtain

$$\ln X \cong \ln N!-(N_1\ln N_1-N_1)-(N_2\ln N_2-N_2)-\ldots \tag{8.4.7}$$

Let us now maximize $\ln X$ with respect to one of the variables, for example N_j, in a manner that is consistent with the constraints of Equations 8.4.1 and 8.4.2. Using the method of Lagrangian multipliers, we obtain, for the most probable occupation number of the jth level, the condition

$$\frac{\partial \ln X}{\partial N_j}+\lambda \frac{\partial N}{\partial N_j}+\mu \frac{\partial U}{\partial N_j}=0. \tag{8.4.8}$$

Upon carrying out the differentiations, we obtain

$$-\ln N_j+\lambda+\mu E_j=0. \tag{8.4.9}$$

That is to say:

$$N_j=e^{\lambda+\mu E_j}=C e^{\mu E_j}. \tag{8.4.10}$$

What now remains is to identify the Lagrangian multipliers λ (or $C=e^{\lambda}$) and μ. Multiply both sides of Equation 8.4.9 by N_j. Recall that i is a running subscript going from 1 to m, and that j is one particular value of i. Therefore now change the subscript from j to i, and sum from $i=1$ to m, and Equation 8.4.9 now becomes

$$-\sum_{i=1}^m N_i \ln N_i+\lambda N+\mu U=0, \tag{8.4.11}$$

where we have made use of Equations 8.4.1 and 8.4.2. From Equation 8.4.7, we see that

$$-\sum_{i=1}^m N_i \ln N_i=\ln X-\ln N!-N, \tag{8.4.12}$$

so that

$$\ln X=\ln N!-(\lambda+1) N-\mu U. \tag{8.4.13}$$

Now apply Equation 8.3.3, followed by Equation 8.3.2, and we immediately make the identification

$$\mu=-\frac{1}{k T}. \tag{8.4.14}$$

Thus Equation 8.4.10 becomes

$$N_j=C e^{-E_j /(k T)}. \tag{8.4.15}$$

We still have to determine C. If we change the subscript in Equation 8.4.15 from j to i and sum from 1 to m, we immediately find that

$$C=\frac{N}{\sum_{i=1}^m e^{-E_j /(k T)}}. \tag{8.4.16}$$

Thus

$$\frac{N_j}{N}=\frac{e^{-E_j /(k T)}}{\sum e^{-E_j /(k T)}} \tag{8.4.17}$$

where I have omitted the summation limits (1 and m) as understood..

However, there is one factor we have not yet considered. Most energy levels in an atom are degenerate; that is to say there are several states with the same energy. Therefore, to find the population of a level, we have to add together the populations of the constituent states. Thus each term in Equation 8.4.17 must be multiplied by the statistical weight ϖ of the level. (This is unfortunately often given the symbol g. See section 7.14 for the distinction between d, g and ϖ. The symbol ϖ is a form of the Greek letter pi.) Thus we arrive at *Boltzmann's Equation*:

$$\frac{N_j}{N}=\frac{\varpi_j e^{-E_j /(k T)}}{\sum \varpi_i e^{-E_i /(k T)}} \tag{8.4.18}$$

The denominator of the expression is called the *partition function* (die Zustandsumme). It is often given the symbol u or Q or Z.

The statistical weight of a level of an atom with zero nuclear spin is $2J+1$. If the nuclear spin is I, the statistical weight of a level is $(2I+1)(2J+1)$. However, the same factor $2I+1$ occurs in the numerator and in every term of the denominator of equation 8.4.18, and it therefore cancels out from top and bottom. Consequently, in working with Boltzmann's equation, under most circumstances it is not necessary to be concerned about whether the atom has any nuclear spin, and the statistical weight of each level in equation 8.4.18 can usually be safely taken to be $(2J+1)$.

In equation 8.4.18 we have compared the number of atoms in level j with the number of atoms in all level. We can also compare the number of atoms in level j with the number in the ground level 0:

$$\frac{N_j}{N_0} = \frac{\varpi_j e^{-E_j/(kT)}}{\varpi_0} \tag{8.4.19}$$

Or we could compare the number in level 2 to the number in level 1, where "2" represent any two level, 2 lying higher than 1:

$$\frac{N_2}{N_1} = \frac{\varpi_2}{\varpi_1} e^{-(E_2-E_1)/(kT)} = \frac{\varpi_2}{\varpi_1} e^{-h\nu/(kT)}. \tag{8.4.20}$$