

## 21.4: Deriving the Boltzmann Equation II

In [Section 20-9](#), we find that the probability of the population set  $\{N_1, N_2, \dots, N_i, \dots\}$  in an isolated system is

$$\rho_{MS,N,E} = N! \prod_{i=1}^{\infty} \frac{g_i^{N_i}}{N_i!}$$

The thermodynamic probability

$$W(N_i, g_i) = N! \prod_{i=1}^{\infty} \frac{g_i^{N_i}}{N_i!}$$

is the number of microstates of the population set.  $\rho_{MS,N,E}$  is the constant probability of any one microstate. In consequence, as we see in [Section 20.10](#), the probability of a population set is proportional to its thermodynamic probability,  $W(N_i, g_i)$ . It follows that the most probable population set is that for which  $W(N_i, g_i)$  is a maximum. Our microscopic model asserts that the most probable population set,  $\{N_1^*, N_2^*, \dots, N_i^*, \dots\}$ , characterizes the equilibrium state, because the equilibrium system always occupies the either the most probable population set or another population set whose macroscopic properties are indistinguishable from those of the most probable one.

Evidently, the equilibrium-characterizing population set is the one for which  $W(N_i, g_i)$ , or  $\ln W(N_i, g_i)$ , is a maximum. Let us assume that the  $N_i$  are very large so that we can treat them as continuous variables, and we can use Stirling's approximation for  $N_i!$ . Then we can use Lagrange's method of undetermined multipliers to find the most probable population set by finding the set,  $N_1, N_2, \dots, N_i, \dots$ , for which  $\ln W(N_i, g_i)$  is a maximum, subject to the constraints

$$N = \sum_{i=1}^{\infty} N_i$$

and

$$E = \sum_{i=1}^{\infty} N_i \epsilon_i.$$

From our definition of the system, both  $N$  and  $E$  are constant. The mnemonic function is

$$\begin{aligned} F_{mn} &= \ln \left( \frac{N! g_1^{N_1} g_2^{N_2} \dots g_i^{N_i} \dots}{N_1! N_2! \dots N_i! \dots} \right) + \alpha \left( N - \sum_{i=1}^{\infty} N_i \right) + \beta \left( E - \sum_{i=1}^{\infty} N_i \epsilon_i \right) \\ &\approx N \ln N - N - \sum_{i=1}^{\infty} N_i \ln N_i + \sum_{i=1}^{\infty} N_i + \sum_{i=1}^{\infty} N_i \ln g_i + \alpha \left( N - \sum_{i=1}^{\infty} N_i \right) + \beta \left( E - \sum_{i=1}^{\infty} N_i \epsilon_i \right) \end{aligned}$$

Taking the partial derivative with respect to  $N_i$  gives

$$\frac{\partial F_{mn}}{\partial N_i} = -N_i \left( \frac{1}{N_i} \right) - \ln N_i + 1 + \ln g_i - \alpha - \beta \epsilon_i = -\ln N_i + \ln g_i - \alpha - \beta \epsilon_i$$

from which we have, for the population set with the largest possible thermodynamic probability,

$$-\ln N_i^* + \ln g_i - \alpha - \beta \epsilon_i = 0$$

or

$$N_i^* = g_i \exp(-\alpha) \exp(-\beta \epsilon_i)$$

We can again make use of the constraint on the total number of molecules to find  $\exp(-\alpha)$  :

$$N = \sum_{i=1}^{\infty} N_i^* = \exp(-\alpha) \sum_{i=1}^{\infty} g_i \exp(-\beta \epsilon_i)$$

so that  $\exp(-\alpha) = Nz^{-1}$ , where  $z$  is the partition function,  $z = \sum_{i=1}^{\infty} g_i \exp(-\beta\epsilon_i)$ . Therefore, in the most probable population set, the number of molecules having energy  $\epsilon_i$  is

$$N_i^* = Nz^{-1} g_i \exp(-\beta\epsilon_i)$$

The fraction with this energy is

$$\frac{N_i^*}{N} = z^{-1} g_i \exp(-\beta\epsilon_i)$$

This fraction is also the probability of finding an arbitrary molecule in one of the quantum states whose energy is  $\epsilon_i$ . When the isolated system and the corresponding constant-temperature system are functionally equivalent, this probability is  $P_i$ . As in the two previous analyses, we have

$$\begin{aligned} P_i &= g_i \rho(\epsilon_i) \\ &= z^{-1} g_i \exp(-\beta\epsilon_i). \end{aligned}$$

This derivation of Boltzmann's equation from  $W_{max}$  is the most common introductory treatment. It relies on the assumption that all of the  $N_i$  are large enough to justify treating them as continuous variables. This assumption proves to be invalid for many important systems. (For ideal gases, we find that  $N_i = 0$  or  $N_i = 1$  for nearly all of the very large number of energy levels that are available to a given molecule.) Nevertheless, the result obtained is clearly correct; not only is it the same as the result of our two previous arguments, but also it leads to satisfactory agreement between microscopic models and the macroscopic properties of a wide variety of systems.

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