3.3: Deriving the Boltzmann Equation I

In Sections 20-10 and 20-14, we develop the relationship between the system entropy and the probabilities of a microstate, $\rho\left(\epsilon_i\right)$, and an energy level, $P_i=g_i\rho\left(\epsilon_i\right)$, in our microscopic model. We find

$$\begin{aligned} S &= -Nk\sum_{i=1}^{\infty} P_i \ln \rho\left(\epsilon_i\right) \\ &= -Nk\sum_{i=1}^{\infty} g_i\rho\left(\epsilon_i\right)\ln \rho\left(\epsilon_i\right) \end{aligned}$$

For an isolated system at equilibrium, the entropy must be a maximum, and hence

$$-\sum_{i=1}^{\infty} g_i\rho\left(\epsilon_i\right)\ln \rho\left(\epsilon_i\right) \tag{3.3.1}$$

must be a maximum. We can use Lagrange's method to find the dependence of the quantum-state probability on its energy. The $\rho\left(\epsilon_i\right)$ must be such as to maximize entropy (Equation 3.3.1) subject to the constraints

$$1=\sum_{i=1}^{\infty} P_i=\sum_{i=1}^{\infty} g_i\rho\left(\epsilon_i\right)$$

and

$$\langle\epsilon\rangle=\sum_{i=1}^{\infty} P_i\epsilon_i=\sum_{i=1}^{\infty} g_i\varepsilon_i\rho\left(\epsilon_i\right)$$

where $\langle\epsilon\rangle$ is the expected value of the energy of one molecule. The mnemonic function becomes

$$F_{mn}=-\sum_{i=1}^{\infty} g_i\rho\left(\epsilon_i\right)\ln \rho\left(\epsilon_i\right)\ +\alpha^*\left(1-\sum_{i=1}^{\infty} g_i\rho\left(\epsilon_i\right)\right)+\beta\left(\langle\epsilon\rangle-\sum_{i=1}^{\infty} g_i\varepsilon_i\rho\left(\epsilon_i\right)\right)$$

Equating the partial derivative with respect to $\rho\left(\epsilon_i\right)$ to zero,

$$\frac{\partial F_{mn}}{\partial\rho\left(\epsilon_i\right)}=-g_i\ln \rho\left(\epsilon_i\right)\ -g_i-\alpha^* g_i-\beta g_i\epsilon_i=0$$

so that

$$\rho\left(\epsilon_i\right)=\exp\left(-\alpha^*-1\right)\ \exp\left(-\beta\epsilon_i\right)$$

From

$$1=\sum_{i=1}^{\infty} P_i=\sum_{i=1}^{\infty} g_i\rho\left(\epsilon_i\right)$$

the argument we use in Section 21.1 again leads to the partition function, z, and the Boltzmann equation

$$P_i=g_i\rho\left(\epsilon_i\right)=z^{-1}g_i\ \exp\left(-\beta\epsilon_i\right)$$