

## 21.3: 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,  $\rho(\epsilon_i)$ , and an energy level,  $P_i = g_i \rho(\epsilon_i)$ , in our microscopic model. We find

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

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

$$-\sum_{i=1}^{\infty} g_i \rho(\epsilon_i) \ln \rho(\epsilon_i) \quad (21.3.1)$$

must be a maximum. We can use Lagrange's method to find the dependence of the quantum-state probability on its energy. The  $\rho(\epsilon_i)$  must be such as to maximize entropy (Equation 21.3.1) subject to the constraints

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

and

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

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

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

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

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

so that

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

From

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

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

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

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