

## Chapter 2

# “Derivation” of Canonical Distribution

By way of illustration, we now give Schrödinger’s “derivation” of the canonical distribution. The argument (roughly) applies to any system, be it classical or quantum. Let the states be enumerated as follows

$$\begin{array}{lcccccccc} \text{State No.} & 1 & 2 & 3 & \dots & l & \dots & \\ \text{Energy} & \epsilon_1 & \epsilon_2 & \epsilon_3 & \dots & \epsilon_l & \dots & \\ \text{Occupation No.} & a_1 & a_2 & a_3 & \dots & a_l & \dots & \end{array} \quad (2.1)$$

The occupation number means the number of systems in the state. Recall that there are  $N$  systems altogether in the ensemble, so

$$N = \sum_{l=1}^{\infty} a_l. \quad (2.2)$$

We also assume that the total energy  $E$  in the ensemble is fixed, so

$$E = \sum_{l=1}^{\infty} a_l \epsilon_l. \quad (2.3)$$

(These sums are actually finite sums, since only a finite number of the  $a_l$ s can be different from zero.) The number of states of this class for the whole ensemble is the number of ways of getting this configuration:

$$P = \frac{N!}{(a_1)!(a_2)! \dots (a_l)! \dots}. \quad (2.4)$$

We seek to find the *most probable* distribution; that is, to maximize  $P$ , subject to the constraints (2.2) and (2.3). Equivalently, we seek to maximize  $\ln P$ . The usual way of solving such a constrained maximization problem is to

introduce Lagrange multipliers. That is, we seek the unconstrained maximum of

$$\ln P - \alpha \sum_l a_l - \beta \sum_l a_l \epsilon_l. \quad (2.5)$$

where  $\alpha$  and  $\beta$  are parameters to be determined. Now in so doing, recall Stirling’s formula,

$$\ln n! \sim n(\ln n - 1), \quad n \rightarrow \infty. \quad (2.6)$$

Varying the occupation numbers (assumed large), we find then the extremum condition

$$\begin{aligned} 0 &= - \sum_l [\delta a_l (\ln a_l - 1) + \delta a_l] - \alpha \sum_l \delta a_l - \beta \sum_l \epsilon_l \delta a_l \\ &= - \sum_l \delta a_l [\ln a_l + \alpha + \beta \epsilon_l]. \end{aligned} \quad (2.7)$$

This must be true for all  $\delta a_l$ , so

$$\ln a_l + \alpha + \beta \epsilon_l = 0, \quad (2.8)$$

or

$$a_l = e^{-\alpha} e^{-\beta \epsilon_l}. \quad (2.9)$$

Thus, from constraint (2.2),

$$N = \sum_l e^{-\alpha - \beta \epsilon_l}, \quad (2.10)$$

and from constraint (2.3),

$$E = \sum_l \epsilon_l e^{-\alpha - \beta \epsilon_l}. \quad (2.11)$$

The average energy per system is

$$U \equiv \frac{E}{N} = \frac{\sum_l \epsilon_l e^{-\beta \epsilon_l}}{\sum_l e^{-\beta \epsilon_l}} = - \frac{d}{d\beta} \ln Z, \quad (2.12)$$

where the partition function is

$$Z = \sum_l e^{-\beta \epsilon_l}. \quad (2.13)$$

The mean fraction of systems in the  $l$  state is

$$\frac{a_l}{N} = \frac{e^{-\beta \epsilon_l}}{Z}. \quad (2.14)$$

Thus, the canonical distribution has emerged as the most probable (overwhelmingly so as  $N \rightarrow \infty$ ) distribution of systems within the ensemble of fixed total energy.