4.6: Statistical Ensembles from Maximum Entropy

The basic principle: maximize the entropy,

$$S=-k_B\sum_n P_n\ln P_n\ . \tag{4.6.1}$$

μCE

We maximize S subject to the single constraint

$$C=\sum_n P_n-1=0\ . \tag{4.6.2}$$

We implement the constraint $C=0$ with a Lagrange multiplier, $\bar{\lambda}\equiv k_B\,\lambda$, writing

$$S^*=S-k_B\,\lambda\,C\ , \tag{4.6.3}$$

and freely extremizing over the distribution $\{P_n\}$ and the Lagrange multiplier λ. Thus,

$$\begin{aligned}\delta S^* &=\delta S-k_B\lambda\,\delta C-k_B\,C\,\delta\lambda\\ &=-k_B\sum_n\Big[\ln P_n+1+\lambda\Big]\delta P_n-k_B\,C\,\delta\lambda\equiv 0\ .\end{aligned}$$

We conclude that $C=0$ and that

$$\ln P_n=-\big(1+\lambda\big)\ , \tag{4.6.4}$$

and we fix λ by the normalization condition $\sum_n P_n=1$. This gives

$$P_n=\frac{1}{\Omega}\qquad,\qquad \Omega=\sum_n\Theta(E+\Delta E-E_n)\,\Theta(E_n-E)\ . \tag{4.6.5}$$

Note that Ω is the number of states with energies between E and $E+\Delta E$.

OCE

We maximize S subject to the two constraints

$$C_1=\sum_n P_n-1=0\qquad,\qquad C_2=\sum_n E_n\,P_n-E=0\ . \tag{4.6.6}$$

We now have two Lagrange multipliers. We write

$$S^*=S-k_B\sum_{j=1}^2\lambda_j\,C_j\ , \tag{4.6.7}$$

and we freely extremize over $\{P_n\}$ and $\{C_j\}$. We therefore have

$$\begin{aligned}\delta S^* &=\delta S-k_B\sum_n\big(\lambda_1+\lambda_2\,E_n\big)\,\delta P_n-k_B\sum_{j=1}^2 C_j\,\delta\lambda_j\\ &=-k_B\sum_n\Big[\ln P_n+1+\lambda_1+\lambda_2\,E_n\Big]\delta P_n-k_B\sum_{j=1}^2 C_j\,\delta\lambda_j\equiv 0\ .\end{aligned}$$

Thus, $C_1=C_2=0$ and

$$\ln P_n=-\big(1+\lambda_1+\lambda_2\,E_n\big)\ . \tag{4.6.8}$$

We define $\lambda_2\equiv\beta$ and we fix λ_1 by normalization. This yields

$$P_n=\frac{1}{Z}\,e^{-\beta E_n}\qquad,\qquad Z=\sum_n e^{-\beta E_n}\ . \tag{4.6.9}$$

GCE

We maximize S subject to the three constraints

$$C_1 = \sum_n P_n - 1 = 0 \quad , \quad C_2 = \sum_n E_n\, P_n - E = 0 \quad , \quad C_3 = \sum_n N_n\, P_n - N = 0 \ . \tag{4.6.10}$$

We now have three Lagrange multipliers. We write

$$S^* = S - k_B \sum_{j=1}^{3} \lambda_j\, C_j \ , \tag{4.6.11}$$

and hence

$$\begin{aligned} \delta S^* &= \delta S - k_B \sum_n \big(\lambda_1 + \lambda_2\, E_n + \lambda_3\, N_n\big)\, \delta P_n - k_B \sum_{j=1}^{3} C_j\, \delta\lambda_j \\ &= -k_B \sum_n \Big[\ln P_n + 1 + \lambda_1 + \lambda_2\, E_n + \lambda_3\, N_n\Big] \delta P_n - k_B \sum_{j=1}^{3} C_j\, \delta\lambda_j \equiv 0 \ . \end{aligned}$$

Thus, $C_1 = C_2 = C_3 = 0$ and

$$\ln P_n = -\big(1 + \lambda_1 + \lambda_2\, E_n + \lambda_3\, N_n\big) \ . \tag{4.6.12}$$

We define $\lambda_2 \equiv \beta$ and $\lambda_3 \equiv -\beta\mu$, and we fix λ_1 by normalization. This yields

$$P_n = \frac{1}{\Xi}\, e^{-\beta(E_n - \mu N_n)} \qquad , \qquad \Xi = \sum_n e^{-\beta(E_n - \mu N_n)} \ . \tag{4.6.13}$$
