統計物理学I 小テスト(6/10) 解答例

Helmholtzの自由エネルギーは $F=E-TS$ より

$$F=\sum_k E_k P_k + k_BT\sum_k P_k \log P_k$$

この自由エネルギーを、確率の規格化条件 $\sum_k P_k = 1$ を考慮して最小化する分布を求める。すなわち、

$$\frac{\partial}{\partial P_j}\left[\sum_k E_k P_k + k_BT\sum_k P_k\log P_k + \tilde{\alpha}\left(\sum_k P_k - 1\right)\right]=0 \qquad (\tilde{\alpha}\text{は未定定数})$$

$$\Rightarrow \sum_k E_k\cdot\frac{\partial P_k}{\partial P_j} + k_BT\left[\sum_k \frac{\partial P_k}{\partial P_j}\log P_k + \sum_k \cancel{P_k}\cdot\frac{1}{\cancel{P_k}}\frac{\partial P_k}{\partial P_j}\right] + \tilde{\alpha}\cdot\sum_k\frac{\partial P_k}{\partial P_j} = 0$$

$$E_j + k_BT\cdot\left[\log P_j + 1\right] + \tilde{\alpha} = 0.$$

$$(+k_BT)\log P_j = -\tilde{\alpha} - E_j - k_BT$$

$$P_j = e^{\alpha}e^{-\frac{E_j}{k_BT}}$$

$$\log P_j = -\frac{\tilde{\alpha}}{k_BT} - \frac{E_j}{k_BT} - 1 = \alpha - \frac{E_j}{k_BT} \qquad \left(\alpha = -\frac{\tilde{\alpha}}{k_BT} - 1\right)$$

$\tilde{\alpha}$を決定するため、確率の規格化条件を考えると、

$$1=\sum_k P_k = e^{\alpha}\sum_k e^{-\frac{E_k}{k_BT}} \qquad \therefore\ e^{\alpha} = \frac{1}{\sum_k e^{-\frac{E_k}{k_BT}}} = \frac{1}{Z}$$

$$\therefore\ P_j = \frac{1}{Z}e^{-\frac{E_j}{k_BT}}$$