4.1. a) $\frac{\partial}{\partial p_i}\left[-\sum_j p_j \ln p_j - \lambda\left(\sum_j p_j - 1\right)\right] = 0$

$$- \ln p_i - 1 - \lambda = 0$$

$$\ln p_i = -(\lambda + 1)$$

$$p_i = e^{-(\lambda+1)} = \text{const} = \frac{1}{N}$$

b) $\frac{\partial}{\partial p_i}\left[-\sum_j p_i \ln p_i - \lambda_1\left(\sum_j p_j - 1\right) - \lambda_2\left(\sum_j p_j a_j - \langle a\rangle\right)\right] =$

$$= \ln p_i - 1 - \lambda_1 - \lambda_2 a_i = 0$$

$$p_i = e^{-(\lambda_1+1) - \lambda_2 a_i}$$

values of λ_1 and λ_2 follow from

$\sum_j p_j = 1$, $\sum_j p_j a_j = \langle a \rangle$

4.2 c) $p_{ij} = p_{xi}\, p_{yj}$

$$S_x = -\sum_i p_{xi} \ln p_{xi}$$

$$S_y = -\sum_j p_{yj} \ln p_{yj}$$

$$S = -\sum_{ij} p_{ij} \ln p_{ij} = -\sum_{ij} p_{xi} p_{yj} \ln(p_{xi} p_{yj})$$

$$= -\sum_{ij} p_{xi} p_{yj} (\ln p_{xi} + \ln p_{yj})$$

$$= S_x + S_y$$

4.2 b) $$S = -\sum_{j_1, \ldots, j_m} p_{j_1}^{(1)} \cdots p_{j_m}^{(m)} \ln\left(p_{j_1}^{(1)} \cdots p_{j_m}^{(m)}\right)$$

$$= S^{(1)} + \ldots + S^{(m)}$$

3.) N atoms are independent $\Rightarrow$ entropy is sum of entropies of individual atoms

<u>for single atom</u>

$p_1 = p_2 = p_3 = 1/3$ $\qquad S = -3\ \frac{1}{3} \ln \frac{1}{3} = \ln 3$

$S_{total} = N \ln 3$

Problem 4:

①

Atoms on a lattice

$N_i \;\hat{=}$ number of atoms on interstitial sites

$$E = \varepsilon N_i$$

$$\Omega = \binom{N}{N_i}\binom{N}{N-N_i} = \binom{N}{N_i}^2$$

$$S = k_B \ln \Omega = 2 k_B \ln \binom{N}{N_i} = 2k_B \ln \frac{N!}{N_i!\,(N-N_i)!}$$

$$= 2k_B \Big[N\ln N - N - N_i \ln N_i + N_i - (N-N_i)\ln(N-N_i) + N - N_i \Big]$$

$$S = 2k_B \Big[N\ln N - N_i \ln N_i - (N-N_i)\ln(N-N_i) \Big]$$

$$= 2k_B N \Big[\ln N - p_i(\ln N + \ln p_i) - (1-p_i)(\ln N + \ln(1-p_i)) \Big]$$

$$S = 2k_B N \Big[-p_i \ln p_i - (1-p_i)\ln(1-p_i) \Big] \qquad p_i = \frac{N_i}{N}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{\varepsilon}\left(\frac{\partial S}{\partial N_i}\right)_N = \frac{2k_B}{\varepsilon}\Big[-\ln N_i - 1 + \ln(N-N_i) + 1 \Big]$$

$$= \frac{2k_B}{\varepsilon} \ln \frac{N-N_i}{N_i} = \frac{2k_B}{\varepsilon} \ln \frac{N\varepsilon - E}{E}$$

$$\frac{\varepsilon}{2k_BT} = \ln \frac{N\varepsilon - E}{E}$$

$$\frac{N\varepsilon}{E} - 1 = e^{\varepsilon/2k_BT}$$

$$\boxed{E = \frac{N\varepsilon}{1 + e^{\varepsilon/2k_BT}}}$$

$$C = \left(\frac{\partial E}{\partial T}\right)_N = \frac{N\varepsilon}{(1 + e^{\varepsilon/2k_BT})^2} \; e^{\varepsilon/2k_BT} \; \frac{\varepsilon}{2k_BT^2}$$

$$\boxed{C = \frac{N\varepsilon^2}{2k_BT^2} \; \frac{e^{\varepsilon/2k_BT}}{(1 + e^{\varepsilon/2k_BT})^2}}$$